On the Mechanism of Cathodic Crystal Growth Processes

B. C. Banerjee and P. L. Walker, Jr. (pp. 449-454, Vol. 108, No. 5)

S. C. Barnes[5]: I have found the paper full of interest, and agree wholeheartedly with the authors that much has yet to be elucidated before we can fully understand the exact mechanism of cathodic crystal growth.

There are, however, one or two points which the authors fail to make clear in the paper, and also many about which further information would be appreciated.

Are we to believe that the 2.5 pH glycine bath produces a hexagonal form of copper?

It would appear so if the preferred orientation is $[10\bar{1}0] + [211]$. Do not the authors think the extra diffraction rings which they have observed, and obviously indexed as hexagonal copper, could possibly have originated from some codeposited impurity?

Shreir and Smith[6] quote an excess deposit weight, above the Faraday theoretical weight, of nearly 6% for a copper deposit obtained from a solution containing only 7.5 g/l glycine. Presumably, at least as much material would be codeposited from a bath containing 25 g/l glycine as used by the authors, probably more.

The authors say nothing about the number of times they used any one portion of electrolyte. Have they observed any difference between, for example, freshly made up glycine baths, and similar baths, after extended use?

Were the complex baths subjected to the low current density pre-electrolysis before, or after, addition of glycine? It is known that this addition agent is used up during electrolysis.[6]

The authors interpret the diffraction patterns originating from the specimens plated in baths [1] and [2] by suggesting that the deposit is of a larger grain size than the substrate. However, under the deposition conditions used (10 ma/cm², 25°C), it is known that deposits from uncontaminated acid-copper sulfate baths continue the substrate structure to thicknesses larger than those investigated by the authors. This has been shown for polycrystalline and single-crystal substrates.[7,9,9] It is difficult to see, therefore, how the deposit grain size could increase substantially after the comparatively short plating times used here. Deposits from glycine-containing solutions have likewise been observed to grow initially epitaxial,[10] although, at 25 g/l of addition agent, they would undoubtedly soon become polycrystalline, with their orientation completely unrelated to the substrate.

Epitaxial copper deposits, formed on the indi-

vidual grains of polycrystalline strip, as well as on single-crystal cathodes, develop low index flat facets at varying angles to the mean substrate surface,[7,11] at times of the order of 30 min.[11,12] Even after plating times shorter than this, it is possible, by electron microscopy, to pick out the genesis of what ultimately become the well-defined crystallites.[11,12] Is it not possible that in their electron diffraction examination the authors have examined only the top few atom layers, and that they have observed these epitaxial crystallites?

In the Discussion section of their paper, the authors make use of the dislocation growth mechanism. This, it should be remembered, was originally proposed to account for the many experimental observations that crystal growth could occur at supersaturations below which, according to earlier theories, repeated nucleation at perfect surfaces was impossible.

In the present case, the supersaturation (as indicated by the overvoltage at the c.d. used, which was not measured) can be expected to be sufficient for repeated nucleation, particularly for those solutions containing large amounts of glycine.[6]

Furthermore, the preparatory treatment used for the copper strip in these experiments would also result in there being available numerous growth sites. The surface would, on an atomic scale, be far from smooth. In fact, it would probably be exceedingly rough. Thus growth could, under the experimental conditions used, continue without the necessity of invoking a dislocation mechanism, although sites at emergent dislocation steps would undoubtedly also contribute to the number of available sink positions. A mechanism suggested by Pick, et al.,[11] involving the "bunching" of growth layers, could be used to explain some of the authors' observations.

More information also would be appreciated on the actual metallurgical state of the substrate materials. Metal strip can have pronounced texture; after high deformations, face centered cubic metals can have, for example, a (110) [12] rolling texture or a (100) [001] annealing texture. In view of the small thickness dimensions of the materials used, it is difficult to visualize them having completely random orientations, unless special rolling and annealing schedules were employed.

Any initial texture would influence the first stages of deposition and, in the case of completely epitaxial deposits, be propagated completely. In fact, most of the early work on the crystal morphology of acid-copper deposits was carried out using base material with a cube texture.[11,14,15,16,17] This work has shown unambiguously that base-deposit continuity can occur over a wide range of deposition conditions.

[5] Joseph Lucas Group Research Centre, The Radleys, Birmingham 33, England.
[6] L. L. Shreir and J. W. Smith, Trans. Faraday Soc., 50, 393 (1954).
[7] G. G. Storey and S. C. Barnes, Trans. Inst. Metal Finishing. 37, 11 (1960).
[8] G. Poli and L. P. Bicelli, Metallurgia Ital., 51, 548 (1959).
[9] S. C. Barnes, Electrochim. Acta, In Press.
[10] G. G. Storey and S. C. Barnes, J. Inst. Metals, In Press.

[11] H. J. Pick, G. G. Storey, and T. B. Vaughan, Electrochim. Acta, 2, 165 (1960).
[12] V. R. Howes, Proc. Phys. Soc. (London), 74, 616 (1959).
[13] T. B. Vaughan, Ph.D. Thesis, University of Birmingham (1959).
[14] H. J. Pick and J. Wilcock, Trans. Inst. Metal Finishing, 35, 298 (1958).
[15] R. Sroka and H. Fischer, Z. Elektrochem., 60, 109 (1956).
[16] H. Seiter and H. Fischer, Z. Electrochem., 63, 249 (1959).
[17] G. G. Storey, Ph.D. Thesis, University of Birmingham (1959).

When this occurs the deposit has, of necessity, the same texture as the base, and it is a two-degree preferred orientation, not a fiber texture.

Do the authors think this effect could be responsible for some of their observations on low c.d. nickel deposits which always seem to have a [110] orientation? The lattice parameters of copper and nickel are only 2.5% different, so thin deposits would probably be epitaxial. It is conceivable that any residual rolling texture in the copper strip cathode material could induce the observed texture in the nickel deposit.

In conclusion, I should like to congratulate the authors on their fine piece of work, but would recommend that as many of the now readily available experimental techniques, which can be used in studies such as these, be used simultaneously. It will be only by correlating chemical, electrochemical, metallurgical, and crystallographic information that a final solution to the complex problem of cathodic crystal growth will be possible.

P. V. K. Porgess[19]: I have found the paper a useful contribution to the complex field of electrodeposition and cathodic crystal growth. There is one point which the authors do not make clear. They state that the 2.5 pH glycine bath produces a copper deposit with a (10$\bar{1}$0) + (211) preferred orientation. In other words, they have interpreted their electron diffraction patterns as being partly due to a new hexagonal copper. They do not, however, give any details as to its crystallography.

Fig. 1 and 2 of this discussion are theoretical electron diffraction patterns for f.c.c. copper having [211] and [111] preferred orientations, calculated using the methods given by Wilman.[19] Comparing these with the authors' electron diffraction photographs (Fig. 6 and 7) from the deposited copper,

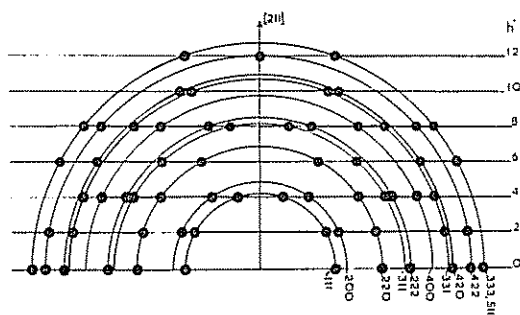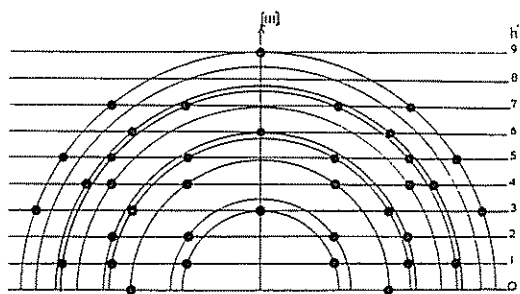[19] Joseph Lucas Group Research Centre, The Radleys, Birmingham 33, England.

Fig. 1

Fig. 2

there seems to be little evidence of a [211] preferred orientation. Their photographs correspond well to a [111] orientation.

Electron diffraction photographs reproduced in journals lose a great deal of fine detail and are therefore difficult to examine properly. If the authors have found extra rings, corresponding to a hexagonal form of copper, which are not visible in the reproductions, then this undoubtedly would be a basis for a very useful paper.

B. C. Banerjee and P. L. Walker, Jr.: Drs. Barnes and Porgess have offered interesting comments on our report of the development of h.c.p. (10$\bar{1}$0) + f.c.c. (211) orientations in electrolytic copper deposits. The following discussion may clarify some of the points raised.

The deposits under discussion were obtained by electrodepositing copper on polycrystalline Cu foils from a complex copper-glycine bath at 25°C and a pH of 2.5. Current density was 10 ma/cm². The diffraction patterns showing the mixed orientations obtained appear in Fig. 6 and 7 of our paper. Surface roughness of the copper deposits, resulting probably from adsorption of organic impurities from the bath even with comparatively small deposit thicknesses, caused losses in intensity, definition, and resolution in the reflection electron diffraction ring patterns. Further losses of definition in the final reproduction of the patterns, particularly the complete invisibility of (400) and (333) ring systems in Fig. 6 and 7, can easily lead to a mistaken interpretation of crystallite orientations in a visual examination of the figures. Hence, we can readily understand the temptation to attribute the characteristics of the published patterns to (111) preferred orientation, rather than a mixed (10$\bar{1}$0) + (211), since the (10$\bar{1}$0) and (111) ring systems are very close to each other. This point is emphasized by recent work on the development of h.c.p. (10$\bar{1}$0) and f.c.c. (211) orientations by electrodeposited nickel, reported by Yang[20] and by Banerjee and Goswami.[21]

Examination of the theoretical patterns for f.c.c. structures furnished by Dr. Porgess shows the (311) and (222) ring systems lying very close to each other. The same is true for the (331) and (420) systems. Such close-lying systems will overlap each other in the absence of good resolution. However, examination of Fig. 6 and 7 shows that a faint (222) ring can, in fact, be detected, lying just beyond the much stronger (311). Careful study of the figures (or better, of the original plates) reveals no intensity maxima (arcing) at the intersection of the (111) normal (orientation axis) with the (222) and (333) ring systems, which should occur if (111) orientation is present. Thus, the evidence is strong that (111) orientation is absent. In drawing the opposite conclusion from our figures, Dr. Porgess may, we feel, have mistaken the (422) ring for the (333). The latter is not visible in the published figures.

[19] H. Wilman, *Acta Cryst.*, 5, 782 (1952).
[20] L. Yang, *This Journal*, 97, 241 (1950).
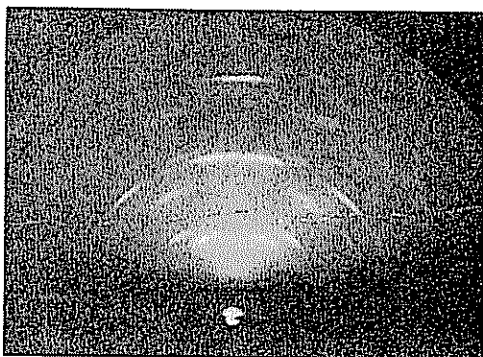[21] B. C. Banerjee and A. Goswami, *J. Sci. Ind. Research* (India), 14B, 322 (1955).

Fig. (A). A reflection electron diffraction pattern showing h.c.p. (10$\bar{1}$0) + f.c.c. (211) orientations for electrodeposited nickel (sulfate chloride bath, pH 5.1, c.d. 10 ma/cm², bath temperature 25°C).
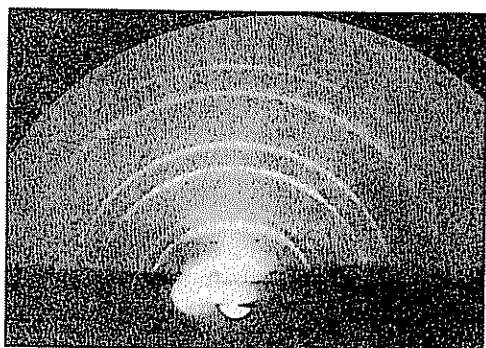

Fig. (B). A fresh reproduction of Fig. 7 in the original paper, showing (10$\bar{1}$0) + (211) preferred orientation for electrolytic nickel.

Intensity maxima (arcing) can clearly be seen on the intersections of the (211) normal (orientation axis) with the (311) and (422) ring systems, in the figures. Therefore, the evidence for (211) orientation is very good. However, since the unit cell dimensions for hexagonal copper are not known, there remains the possibility that second order reflections from (10$\bar{1}$0) planes could be falling approximately on the (311) ring. This possibility is strengthened considerably by the marked similarity of the patterns in Fig. 6 and 7 to those for electrodeposited nickel in which mixed structures have been established to be present. Fig. (A) published here shows a mixed structure of the electrolytic nickel for comparison with Fig. (B) which is a fresh reproduction of Fig. 7 in the original paper. More work remains to be done on the structure of the copper deposits, but the present evidence, in our opinion, definitely favors the presence of mixed structures.

The development of mixed structures in nickel has been attributed[22,23] to twinning introduced into the deposits during the growth process, caused by adsorption of impurities such as hydrogen or hydroxides. Similar considerations may hold in the case of copper. A second effect may arise from impurities such as those generated at the catholyte layer. These may hinder the mobility of atoms deposited on the cathode surface, which, in turn, may

affect the manner in which they are incorporated into the crystal lattice.

Regarding purification of the plating solutions and the consumption of glycine resulting from repeated use, it can be stated that the acid-copper solutions were purified by prolonged low-current electrolysis using a dummy cathode, after which glycine was dissolved in the purified solution. This was followed by repeated filtration to remove suspended impurities. Fresh solutions from stock prepared in this way were used for electrodeposition, the used solutions being discarded after each experiment.

The current density used, 10 ma/cm², was not high enough to produce a large supersaturation of the ionic species at the catholyte layer. Hence, a dislocation growth mechanism must be considered to be important, although repeated nucleation may also have been occurring. However, we would like to point out that the dislocation growth mechanism may be important even at considerably higher current densities. The reason for this is that an impoverishment of metal ions will occur in the cathode-solution interfacial region, so that supersaturation of the metal ions may be comparatively low even though the current is large. Under these conditions, one finds that species other than the metal are also being deposited.

We completely agree with Dr. Barnes that a cathode surface can hardly be considered to be atomically smooth, and it may contain numerous imperfections or structural inhomogeneities that may be responsible for development of undulations of various sizes and shapes, at later stages of deposition. But the shapes of these undulations are not likely to be exact replicas of the microscopic inhomogeneities present in the original cathode surface.

Several factors besides the bath conditions and the structural imperfections in the original cathode surface are likely to influence the mechanisms of cathodic crystal growth. The following may be mentioned: (a) high porosity of the electrodeposits, especially in the early stages of deposition;[22] (b) the exothermic character of the electrodeposition process;[22] (c) influences of the considerable internal stresses developed in electrodeposits at various stages of deposition;[22,23] (d) influences of bath impurities;[24] and (e) the possibility of solid state reactions occurring at the surfaces of growing deposits. For a complete understanding of the complex processes involved in electrocrystallization, all of these factors must be explored. We hope that our work, though limited in scope, is a helpful contribution to the knowledge of electrodeposition phenomena.

Acknowledgment

[22] H. Wilman, *Proc. Phys. Soc. (London)*, 68B, 474 (1955).
[23] I. L. Newell, *Metal Finishing*, pg. 56, Oct. 1960.
[24] B. C. Banerjee and A. Goswami, *J. Sci. Ind. Research (India)*, 16B, 144 (1957).