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Electrocrystallization of zinc on copper single crystal planes under the influence of an asymmetric alternating current

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Zinc electrodeposited from a sulphate bath on to copper single crystal planes revealed a layer-type growth on copper (1 1 1) and (1 0 0) planes and ridge-type growth on the (1 1 0) plane at low d.c. densities. Dendritic growth appeared at higher d.c. densities on all the planes. Superimposition of a.c. on d.c. during electrocrystallization produced hexagonal pyramids on the copper (1 1 1) plane, which were transformed into hexagonal dendrites under suitable a.c. to d.c. ratios. The influence of a.c. on the degree of epitaxy of zinc on copper and the mechanism of the dendrite initiation are discussed.

1. Introduction

Epitaxy in crystal growth is a phenomenon well known for its technical utility [1]. Epitaxial systems cover a wide range of metals and metallic compounds [2] and the hetero-epitaxy of zinc on copper single crystal planes is well established. X-ray and electron diffraction studies of the initial zinc electrodeposits showed an epitaxial relationship with copper single crystalline substrates [3, 4]. Morphological features of zinc electrodeposits on copper single crystals, observed earlier by Keen and Farr [5] and recently in our laboratory [6] also provide evidence for the epitaxial growth of zinc on copper singel crystals. It is known that epitaxial growth in electrocrystallization is governed by the crystallographic nature of the substrate and the bath conditions. Alternating current is found to influence the growth conditions during electrodeposition and has been advantageously used to improve the epitaxy in zinc, cadmimum, tin and lead electrodeposits [7, 8]. In this paper, a microscopic observation of the various morphological features of zinc electrodeposits on copper single crystals, obtained at different d.c. densities and in the presence of superimposed a.c. are presented. On the basis of these observations an attempt is made to explain the influence of asymmetric a.c. on the degree of epitaxy of zinc on copper single crystal planes.

Dendritic growth in electrodeposited zinc from alkaline zincate solution is extensively studied with respect to the mechanism of its initiation and propagation [9]. Crystallographic and morphological studies of electrolytic zinc dendrites grown from alkaline zincate solutions have been reported [10]. The influence of superimposed a.c. at the moment of initiation of dendritic growth from the sulphate bath seems to give a clue to the mechanism of its initiation and hence is also reported here.

2. Experimental

A high voltage battery was used as a constant d.c. source. Alternating current (50 Hz) drawn from mains with suitable adjustments to maintain a galvanostatic condition, was superimposed on the d.c. by means of a circuit described earlier [11]. As the rippling current ($I_{\text{a.c.}} < I_{\text{d.c.}}$) and pulsating current ($I_{\text{a.c.}} = I_{\text{d.c.}}$) indicated no substantial effect on the electrocrystallization, the effect of current with an anodic component ($I_{\text{a.c.}} > I_{\text{d.c.}}$) was investigated. The a.c. densities were calculated from the absolute values of the strength of the current passing through the cell. The preparation of the cathode surface, electrolytic cell and general procedures have been described elsewhere [6].

Zinc sulphate–ammonium sulphate baths of composition 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ and 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ were used to deposit zinc on copper single crystal planes. The thickness of the deposit was maintained constant at 5 C cm^{-2} before the initiation of dendrites. After the initiation of dendrites, the deposit time was chosen as appropriate for the desired dendrite morphologies. Overpotential was recorded with an accuracy of ± 5 mV using a VTVM. The cathodes were removed without switching off the current and washed well with conductivity water and then with ethyl alcohol. The surfaces of the deposits were microscopically examined. Each experiment was repeated to ensure reproducibility.

3. Results

Copper (1 1 1), (1 0 0) and (1 1 0) planes were employed as substrates for deposition. Deposition of zinc was carried out at different d.c. densities from a 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath. Morphological features observed at these current densities and the corresponding overpotential values recorded were as follows.

At 5 mA cm^{-2}, zinc electrodeposits on all the planes consisted of patches of mossy and granular growth. Apart from the mossy type, the growth on the (1 1 1) and (1 0 0) planes resembled layers with irregular edges and was ridge-type on the (1 1 0) plane. The overpotential at this current density was in the range of 50 to 60 mV on all the planes. Within the first minute of deposition, the over-potential reached a maximum and then showed a decreasing trend marking the onset of mossy growth [8].

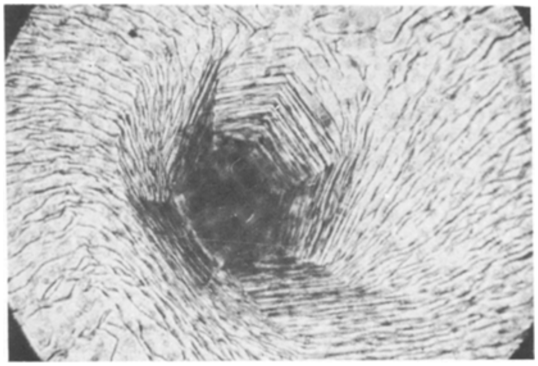

Figure 2 Hexagonal pyramid on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c. density = 10 mA cm^{-2}, × 300.

The electrodeposits at 10 mA cm^{-2} were devoid of mossy growth. Deposits completely covered the surface, were uniform and showed distinct morphological patterns. The deposit on the (1 1 1) plane exhibited a layer-type growth (Fig. 1), with occasional large hexagonal pyramids (Fig. 2). Morphology on the (1 0 0) plane was also of the layer-type (cf. Fig. 1), where as fine ridges (Fig. 3) characterized the deposits on the (1 1 0) plane. At this current density, overpotential values fell to 80 to 100 mV on all planes.

The overpotential observed at 20 mA cm^{-2} was large, ranging from 400 to 500 mV on all the planes. However, there was a gradual increase in overpotential during deposition beginning about 100 mV and reaching the maximum value of 500 mV after 2 min deposition. After this slight fluctuations occurred. This marked the initiation of dendritic growth. After a deposition thickness

Figure 1 Layer growth of zinc observed on Cu (1 1 1) and Cu (1 0 0) planes. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c. density = 10 mA cm^{-2}, × 300.

Figure 3 Ridge-type growth on a Cu (1 1 0) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c. density = 10 mA cm^{-2}, × 600.

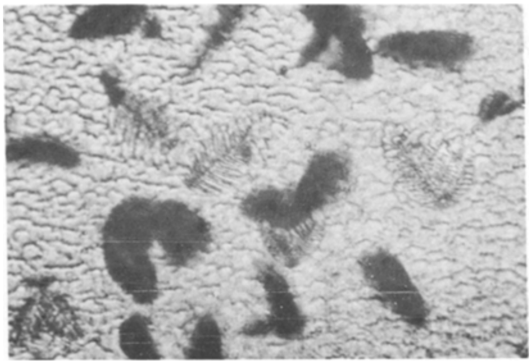

Figure 4 Dendritic growth in a background of layers interspersed among dark blocks observed on Cu (1 1 1) and Cu (1 0 0) planes. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c. density = 20 mA cm^{-2}, × 600.

5C cm^{-2} was reached, classical two-dimensional dendrites with a background of layers interspersed among dark blocks (Fig. 4) were observed on the (1 1 1) and (1 0 0) planes, whereas on the (1 1 0) plane only blocks were seen.

At 25 mA cm^{-2} there was a spontaneous evolution of gas on the surface. The overpotential shot instantaneously to a value of 600 to 700 mV and exhibited major fluctuations. The surface was covered with a spongy deposit. When the crystal was removed after 2 min deposition and examined, well developed classical two-dimensional dendrites in a background of black sponge (Fig. 5) were observed. This occurred on all the planes. Above 25 mA cm^{-2}, the deposits were in the form of a thick dendritic sponge.

The experiments were performed at the same current densities for the 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath. The dendritic growth was found to initiate at 15 mA cm^{-2}. The morphology before dendrite initiation (at <15 mA cm^{-2}), was very much the same as that observed in the former bath, but epitaxial growth was poorer by comparison. The overpotential values from this bath were higher compared to those for the former bath at corresponding current densities. However, dendritic growth appeared to be more facile in this bath. Well developed dendrites, as shown in the microphotographs, grew from this bath.

3.1. Deposit morphology under the influence of superimposed a.c. on d.c.

Asymmetric a.c. with an anodic component ($I_{a.c.} > I_{d.c.}$) was used throughout. It has been found that the effectiveness of superimposed a.c. on the deposit morphology was enhanced when the a.c. was superimposed on those d.c. values which initially produced good deposits. Hence to study the influence of a.c. on the deposit morphology before dendrite initiation, a d.c. density of 10 mA cm^{-2} and a bath composition of 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ were selected. To study the effect of a.c. on dendrite growth, a d.c. density of 15 mA cm^{-2} and the bath 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ were preferred.

3.2. Deposit morphology at 10 mA cm^{-2} d.c. and various magnitudes of superimposed a.c. from a 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath

Deposition was carried out on the different planes at the following d.c./a.c. ratios: 10 mA cm^{-2}/15 mA cm^{-2} 10 mA cm^{-2}/20 mA cm^{-2}, 10 mA cm^{-2}/25 mA cm^{-2}, and 10 mA cm^{-2}/50 mA cm^{-2}. The deposit morphologies observed in the

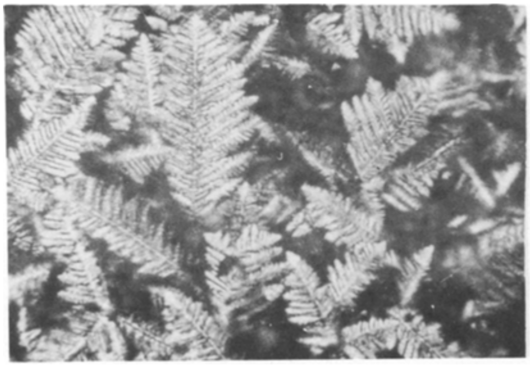

Figure 5 Classical two-dimensional dendrites in a dark spongy background observed on Cu (1 1 1), Cu (1 0 0) and Cu (1 1 0) planes. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c. density = 15 mA cm^{-2}, × 600.

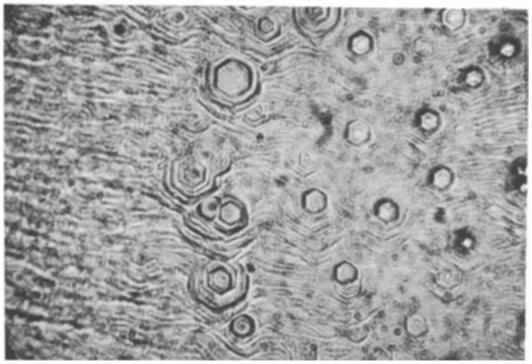

Figure 6 Regular hexagonal pyramids on Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 10 : 15 mA cm^{-2}, × 300.

Figure 7 Hexagonal pyramids on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 10:20 mA cm^{-2}, × 600.

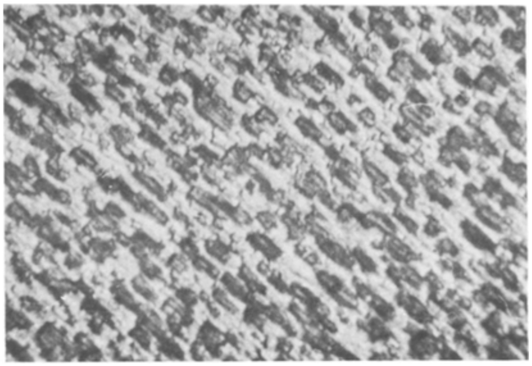

Figure 9 Ridges with rectangular blocks on a Cu (1 1 0) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 10:25 mA cm^{-2}, × 600.

above d.c./a.c. ratios on the different planes, are given below.

(1 1 1) planes. Layers with regular and symmetrical hexagonal pyramids (Fig. 6) were observed at 10 mA cm^{-2} d.c./15 mA cm^{-2} a.c. At 10 mA cm^{-2} d.c./20 mA cm^{-2} a.c., the density of hexagonal pyramids increased (Fig. 7). The shape of the hexagonal pyramids was distorted (rounded) at 10 mA cm^{-2} d.c./25 mA cm^{-2} a.c. (Fig. 8). Random deposit resulted at 10 mA cm^{-2} d.c./50 mA cm^{-2} a.c.

(1 0 0) plane. Compact layers were found (cf. Fig. 1) to develop at the ratios 10 mA cm^{-2} d.c./ 15, 20 and 25 mA cm^{-2} a.c. At 10 mA cm^{-2} d.c./ 50 mA cm^{-2} a.c. the deposit was randomly disposed.

(1 1 0) plane. Fine ridges (cf. Fig. 3) observed at 10 mA cm^{-2} d.c. thickened with increasing ratio of superimposed a.c. At 10 mA cm^{-2} d.c./25 mA cm^{-2} a.c., thick ridges with rectangular blocks (Fig. 9) were observed. At 10 mA cm^{-2} d.c./50 mA cm^{-2} a.c. and above, complete distortion in the ridge pattern produced a random deposit.

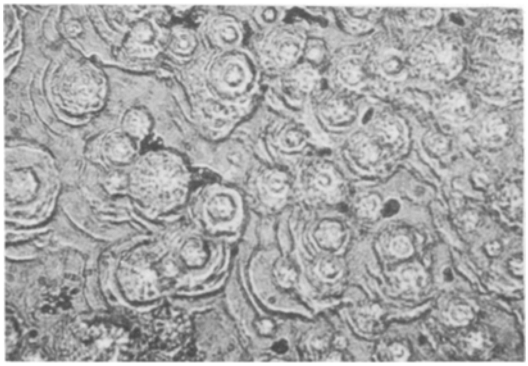

Figure 8 Distorted pyramids on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.1 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 10:25 mA cm^{-2}, × 600.

From the above observations, it was found that the ratio 10 mA cm^{-2} d.c./20 mA cm^{-2} a.c. yielded the clearest results. The overpotential values were less than those observed in pure d.c.

3.3. Influence of superimposed a.c. on dendritic growth

Electrodeposits obtained from 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath at 15 mA cm^{-2} d.c. contained classical two-dimensional dendrites interspersed among dark blocks on the (1 1 1) and (1 0 0) planes (cf. Fig. 4). Only dark blocks appeared on the (1 1 0) plane. The overpotential value ranged from 400 to 500 mV. An alternating current density of 20 mA cm^{-2} was superimposed at this stage. The overpotential value reduced to 250 mV. No dark blocks appeared on the electrodeposits. Figs. 10a and b, 11 and 12a and b show the dendritic growth observed after 1, 2 and 3 min deposition on the (1 1 1) plane, respectively. Fig. 10a and b show the initial growth stage of the dendrites; Fig. 11 shows a hexagonal dendrite initiating from the tip of a hexagonal pyramid whose entire form is shown in Fig. 12a and b. Single fern-like dendrites, and often two dendrites initiating from the same point (Fig. 13) were also observed on the (1 1 1) and (1 0 0) planes. No hexagonal star-shaped dendrites appeared on the (1 0 0) and (1 1 0) planes. The dendrites that appeared on the (1 1 0) plane after 1 min deposition were all aligned along [1 1 0] direction (Fig. 14). When the magnitude of superimposed a.c. was increased to 30 mA cm^{-2}, a network-like pattern was observed on the (1 1 1) plane (Fig. 15). A

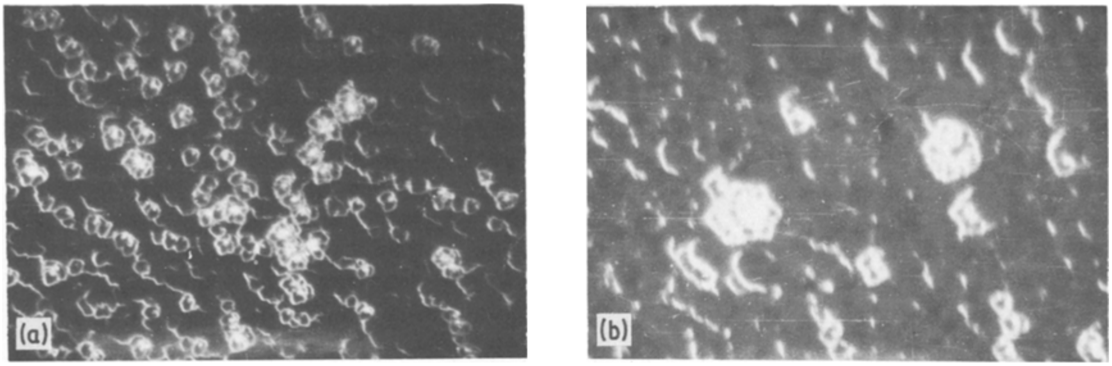

Figure 10 (a) and (b) Initiation of dendirtes from screw dislocations on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 15 : 20 mA cm^{-2}. Dark-field illumination, × 600.

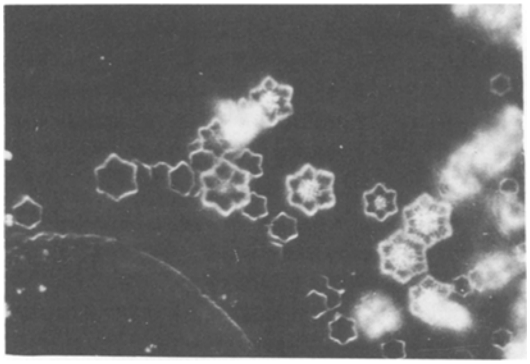

Figure 11 Dendrites initiating at the tip of a hexagonal pyramid on a Cu (1 1 1) plane 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 15 : 20 mA cm^{-2} for 2 min. Dark-field illumination, × 600.

further increase in the magnitude of the superimposed a.c. resulted in a random deposit, thus leading to an elimination of the dendritic growth. The time of deposition in all these experiments die not exceed 3 min.

4. Discussion

A survey of the results indicate that the morphology of zinc on copper single crystal planes follows the same trend as observed in alkaline zincate solution [9]. At low current densities and corresponding low overpotentials, mossy deposits develop. At higher current densities and corresponding overpotentials, dendritic growth results. Between the above two current densities and the corresponding overpotentials, granular growth appears. This suggests that the conditions necessary for the appearance of the above mentioned morphological features are also met with in the sulphate bath. However, the critical values at which a particular growth feature initiates differ from those observed from alkaline zincate solution.

According to Oxley *et al.* [12], dendrites form at lower current densities from solutions of highly viscous zincate-saturated sodium hydroxide solution than from zincate-saturated potassium hydroxide solution. It is observed here that the

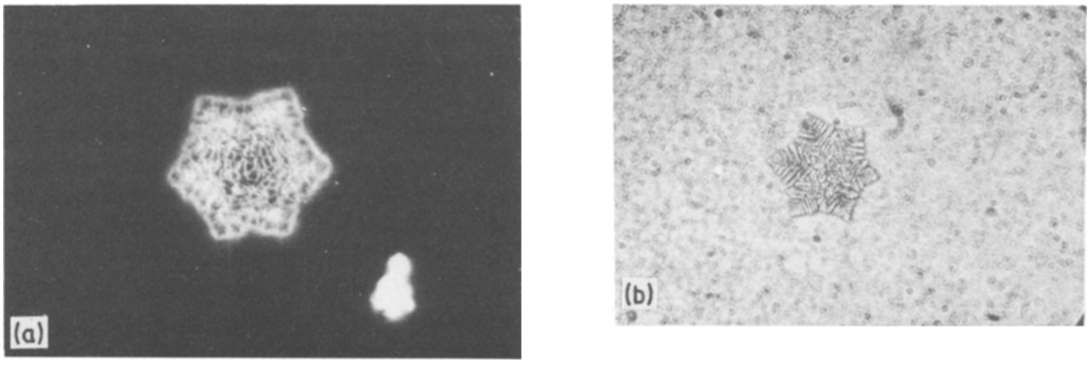

Figure 12 (a) and (b) Hexagonal star-like dendrites on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 15 : 20 mA cm^{-2} for 3 min, × 600. (a) Dark field, (b) bright field.

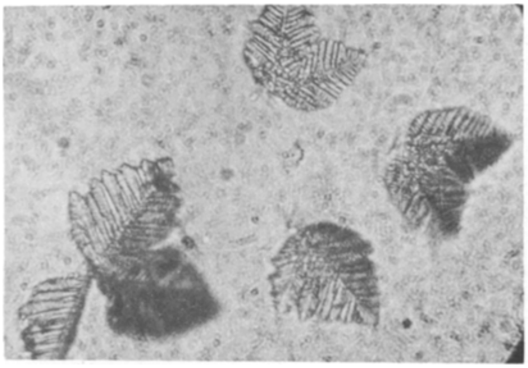

Figure 13 Single fern-like dendrites and two fern-like dendrites initiating at the same point seen on Cu (1 1 1) and Cu (1 0 0) planes. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$; d.c./a.c. ratio = 15 : 20 mA cm^{-2}, × 600.

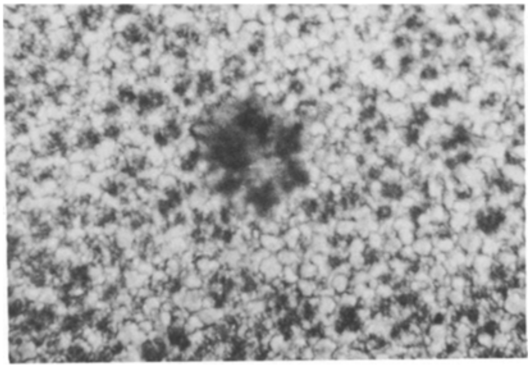

Figure 15 Disappearance of dendritic growth observed on a Cu (1 1 1) plane. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 15 : 30 mA cm^{-2}, × 600.

Figure 14 Dendritic growth aligned along the [1 1 0] direction on a Cu (1 1 0) plane. 0.25 M $ZnSO_4$ + 0.5 M $(NH_4)_2SO_4$ bath; d.c./a.c. ratio = 15 : 20 mA cm^{-2}, × 600.

dendrites initiate with greater facility, at comparatively lower current density from the viscous 0.25 M $ZnSO_4 + (NH_4)_2SO_4$ bath than from the less viscous zinc sulphate solution containing 0.1 M $(NH_4)_2SO_4$.

Granular growths observed at intermediate current densities on different planes are predominantly in the form of layers on (1 1 1) plane, only layers on (1 0 0) and ridges on the (1 1 0) plane because of the epitaxial relationship that exists between the deposit and the substrate [5].

4.1. Epitaxy and the influence of superimposed a.c. on epitaxy

As hetero-epitaxy is the phenomenon of oriented growth of one substance on the crystal of a foreign substrate, the lattice of the deposited metal should orientate itself in such a manner with respect to the substrate that the best fit should result. The orientation of the deposit will be determined by the interfacial free energies involved [13]. This will be minimized by having the close packed directions parallel, and the basal plane parallel to the low index plane. This effect minimizes the misfit. In electrodeposition, the epitaxy is considered to be probably due to the higher kinetic energy and the surface mobility of the adsorbed metal ions [14], as they have a direct bearing on the interfacial free energy. Hence any physical agency that improves the surface mobility of adsorbed metals ions, should also enhance the degree of epitaxy.

In the case of zinc electrodeposits on copper, the preferred orientational relationships are as follows:

$$\mathrm{Zn}\,(0\,0\,0\,1)\,[1\,1\,\bar{2}\,0]\,/\!/\,\mathrm{Cu}\,(1\,1\,1)\,[1\,\bar{1}\,0],$$

$$\mathrm{Zn}\,(0\,0\,0\,1)\,[1\,1\,\bar{2}\,0]\,/\!/\,\mathrm{Cu}\,(1\,0\,0)\,[0\,1\,1],\,[1\,\bar{1}\,0]$$

$$\text{and } \mathrm{Zn}\,(2\,\bar{2}\,0\,5)\,[1\,\bar{1}\,2\,0]\,/\!/\,\mathrm{Cu}\,(1\,1\,0)\,[1\,\bar{1}\,0]\ [4].$$

The epitaxial morphology in a homo- or hetero-epitaxial system is mainly layers and pyramidal type on the (1 1 1) and (1 0 0) planes in fcc, and (0 0 0 1), $(1\,1\,\bar{2}\,0)$ in hcp systems. Ridge-type morphology develops on the (1 1 0) in fcc and $(2\,\bar{2}\,5\,0)$ in hcp system because of the similarity in arrangement of surface atoms on these planes of the two systems.

Layer growth is explained as a bunching of monatomic steps. The microsteps are considered to arise from misorientations of the surface from the crystal plane [15] and dislocations [16]. Recently, Bockris *et al.* [17] have confirmed the hypothesis that the origin of the microsteps is indeed the crystallographic orientation, rather than pairs of dislocations. Pyramids are, however, known [18] to grow from pairs of screw dislocations. Ridge formation is a different form of layer growth.

It is known that electrodeposit characteristics such as adherency, compactness, depend, to a certain extent, upon the epitaxial relationship of these deposits with the substrate in the initial stages of deposition. Superimposed a.c. has been a valuable tool in the improvement of the above characteristics, thereby suggesting a favourable influence on epitaxy. It is contended that the anodic component of superimposed a.c. is mostly responsible in influencing the deposit characteristics [19].

In the present study, the d.c. density ranges which produced granular growth, exhibited only layer-type morphology on the (1 1 1), (1 0 0) and (1 1 0) planes (layers are here called ridges). Under the influence of suitable values of superimposed a.c. (determined experimentally), the electrodeposits not only improved in clarity but also exhibited a predominantly hexagonal pyramidal growth morphology on the (1 1 1) plane and block growth (truncated pyramids) on the (1 1 0) plane.

Layers and pyramids are both epitaxial morphologies. In the present work it was found that the deposit grows epitaxially both during deposition in pure d.c. and in the presence of superimposed a.c. The effect of superimposed a.c., therefore, could be expressed in terms of the degree of epitaxy conferred on the deposits. As the morphologies of deposits obtained from pure d.c. (layers) and those obtained under the influence of superimposed a.c. (pyramidal) are different, they could be related to the degree of epitaxy. It seems plausible to assume that the pyramidal growth morphology represents closer epitaxy on the grounds that it is produced under the influence of superimposed a.c. which is already known to influence epitaxy favourably (in a suitable ratio to d.c.). Secondly, the pyramid shapes are a better exhibition of the symmetry of the substrate lattice (namely, hexagonal pyramids on the (1 1 1) plane).

Although the (0 0 0 1) plane of zinc fits on both the (1 1 1) and (1 0 0) planes of copper [4], it is observed that only layers predominate on the (1 0 0) plane during deposition in pure d.c. and under the influence of superimposed a.c., indicating that, on the basis of the above argument, epitaxial growth does not occur to the same degree as on the (1 1 1) plane.

With regard to the formation of pyramidal growth under the influence of superimposed a.c., it is felt that the anodic component of superimposed a.c. while dissolving the impurities in its wake, may not only provide a greater flux of adsorbed species, but also fade away the macrosteps helping the operation of screw dislocations in the ensuing cathodic cycles. Thus the epitaxy is shown to improve under the influence of superimposed a.c. Optimum values of a.c. were found necessary for good results. Higher magnitudes of superimposed a.c. accompanying higher anodic components had a destructive effect on morphology and hence produced random deposits.

4.2. Dendrite initiation

Dendritic growth centres may develop on growth planes by either screw dislocations, or foreign particles, or two-dimensional nucleation [20]. According to the model proposed by Diggle *et al.* [21], the dendrites originate from the tips of pyramids arising as a result of the rotation of a screw dislocation, but according to the observations of Mansfeld and Gilman [22], dendrites grow instantly between pyramids. However, our observations of zinc dendrites on the copper (1 1 1) plane during deposition under the influence of superimposed a.c. clearly show that screw dislocations are the source of dendrites (cf. Fig. 10a and b). It is evident from Fig. 11 that the dendrites emanate from screw dislocations at the tip of the pyramids. Because the epitaxy improves under the influence of superimposed a.c., the orientating influence of the substrate also becomes conspicuous, and hence the dendrites under the influence of superimposed a.c. propagate in the directions of the six corners of a hexagon and assume a hexagonal star-like form (cf. Fig. 12a and b). Under similar conditions, no star-like hexagonal dendrites were observed on the (1 0 0) and (1 1 0) planes. On the (1 1 0) plane, no evidence of dendrites initiating from screw dislocations was found. The dendrites which nucleated in the initial stage, however, were all oriented along the [1 1 0] direction, indicating the orientating influence of substrate on dendritic growth under the influence of superimposed a.c. The dendrite initiation and growth forms described were again observed at an optimum value of superimposed a.c. Higher values of superimposed a.c. led to the cessation of the dendrite growth.

5. Conclusions

(1) Epitaxy of zinc electrodeposits on copper single crystals improves under the influence of an optimum value of superimposed a.c.

(2) Dendrites emanate from screw dislocations at the tip of pyramids.

Acknowledgements

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References

1. P. HARTMAN, "Crystal Growth: an introduction", edited by W. Bardsley, D. T. J. Hurle and J. B. Mullin, Series in Crystal Growth (North Holland, Amsterdam, 1973) p. 1.
2. MATTHEWS JOHN WANCHOPE, "Epitaxial Growth" (Academic Press, New York, 1975) p. 611.
3. A. GOSWAMI, *Indian J. Pure Appl. Phys.* 7 (1969) 232.
4. ITOH SATOSHI, OKADA GENJI and TETSURO SEIYAMA, *Denki Kagaku Oyobi Kogyo Butsure Kagaku* **242** (1974) 4215.
5. J. M. KEEN and J. P. G. FARR, *J. Electrochem. Soc.* **109** (1962) 668.
6. B. S. SHESHADRI and T. H. V. SETTY, *Electrochim. Acta* 17 (1972) 1895.
7. ST. ANDUROV and N. STOICHEV, *Rost. Kristallov. Akad. Nauk. SSSR Inst. Kristallogr.* 5 (1965) 136.
8. M. F. AHMED, B. S. SHESHADRI and F. PUSHPANADEN, *J. Electrodepos. Surface Treat.* 3 (1975) 65.
9. A. FLEISCHER and J. J. LANDER, "Zinc-silver oxide batteries" (Wiley, New York, 1972) p. 63.
10. J. W. DIGGLE, R. J. FREDERICKS and A. C. REIMSCHUESSEL, *J. Mater. Sci.* 8 (1973) 79.
11. B. S. SHESHADRI and T. H. V. SETTY, *J. Crystal Growth* **21** (1974) 110.
12. J. E. OXLEY and C. W. FLEISCHMANN, "Improvement of zinc electrodes for Electrochemical cells", First quarterly report, Contract NAS 5-9591 (1965) p. 21.
13. N. H. FLETCHER and K. W. LODGE, "Epitaxial Growth", edited by M. J. Wanchope (Academic Press, New York, 1975) p. 555.
14. K. L. CHOPRA, "Thin Film Phenomena" (McGraw-Hill, New York, 1969) pp. 44, 232.
15. A. DAMJANOVIC, M. PAUNOVIC and J. O'M. BOCKRIS, *J. Electroanal. Chem.* 9 (1965) 93.
16. N. CABRERA and D. A. VERMILYEA, "Growth and Perfection of Crystals", edited by R. H. Doremus, B. W. Roberts and D. Turnbull (Wiley, New York, 1958) p. 393.
17. J. O'M. BOCKRIS, Z. NAGY and D. DRAZIC, *J. Electrochem. Soc.* **120** (1973) 30.
18. W. K. BURTON, N. CABRERA and F. C. FRANK, *Phil. Trans. Roy. Soc. (London)* **243** (1951) 299.
19. A. A. SUTYAGINA and K. M. GORBUNOVA, "Soviet Electrochemistry", Vol. II, (Consultants Bureau, New York, 1961) p. 39.
20. R. W. POWERS, "Plating from Alakaline Solutions", Progress Report No. 2 (1967) ILZRO Project No. ZEI20.
21. J. W. DIGGLE, A. R. DESPIC and J. O'M. BOCKRIS, *J. Electrochem. Soc.* **116** (1969) 1503.
22. F. MANSFELD and S. GILMAN, *ibid* **117** (1970) 1521.

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