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Crystallographic and morphological studies of electrolytic zinc dendrites grown from alkaline zincate solutions

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Electrolytic zinc dendrites grown potentiostatically from a range of alkaline zincate solutions were studied using X-ray diffraction and scanning electron microscopy (SEM) to reveal structural and morphological characteristics as a function of their growth rate.

Conclusions from this work were as follows:

Dendrites grown at a rate of 3 μm min^{-1} were identified as twinned monocrystalline "swords" with a noticeable absence of regular branching.

Dendrites grown at a rate of 24 μm min^{-1} were basically twinned monocrystals with some polycrystalline character. As for the slowest growing dendrites, the morphological character was of a sword-like nature. Morphologically these first two types of dendrites show great similarity to the butterfly dendrites of DeVries.

Dendrites grown at 67 μm min^{-1} were of the fern-like morphological type with a large degree of polycrystalline character. These dendrites are suggested as being composites of very small slow growth rate dendrites in a roof tile arrangement.

The results for the ideal fern-like dendrites seemingly disagree with the earlier hcp dendrite work of Wranglen who identified this type of dendrite as a monocrystal. An explanation for this discrepancy is offered.

The work presented here appears to be consistent with the twin plane re-entrant edge (TPRE) growth mechanism.

1. Introduction

Over the last few years there have been several attempts to identify the detailed crystallographic nature of metallic dendrites. Inspection of this literature shows that there is some doubt whether dendrites possess a general crystallographic nature. i.e. are all single crystals as reported by Wranglen [1], or whether their crystallographic nature depends upon (a) lattice type and (b) conditions of growth.

Numerous investigators employing X-ray diffraction techniques have reported dendrites to be single crystals [1, 2], whereas others [3-5] have reported the presence of twin planes (single and multiple). Faust and John [3] proposed a general dendritic growth mechanism based upon a twin plane re-entrant edge (TPRE) concept and developed general rules for when, and when not, a TPRE mechanism was possible. The re-entrant edge simply provides a point for easy nucleation of new growth layers.

Application of the above rules to the hcp lattice, e.g. zinc and cadmium, indicates that, in the usual case, only when the twin plane, the faceting plane and the growth direction coincide will a TPRE mechanism operate. Hcp twinned structures have been reported by Poli and Bicelli [6] for electrodeposited Cd and for Cd "spear" dendrites from the vapour phase [8]. A reinvestigation of those metal dendrites that were

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initially identified as single crystals [1, 2] it has been suggested [7], may reveal them to contain one or more twin planes on the supposition that twinning can easily be overlooked in X-ray diffraction work due to the narrowly spaced lamellae involved; sectioning and etching usually being necessary to reveal twinning.

In the cases where a twin plane forms a bounding surface, the presence of twinning can be tentatively identified with the scanning electron microscope (SEM) [9]. A simple example of this type of twin plane is shown in Fig. 1, where any number of odd twin planes can form the spine of a dendrite whose cross-section is V-shaped.

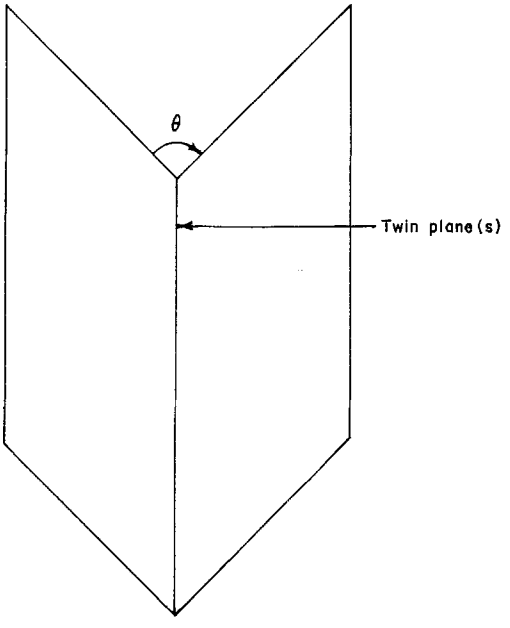


Figure 1 Schematic representation of an odd-numbered twin plane structure similar to the dendrites in this and other work.

The essential role of twinning in the growth mechanism of electrolytic metal dendrites has yet to be demonstrated. The presence of twinning has however been ascertained, but, if the twins can be identified as normal deformation planes then the twinning cannot be assumed as being essential to the growth mechanism. In one case, Cd dendrites [8] from the vapour phase of a leaf-like morphology, twins other than deformation twin planes have been found and thus in this instance twinning must form an essential part of the growth mechanism. In other cases [5, 19], twinning has been identified as occurring after the main growth event.

Faust [7] has suggested that narrowly spaced twinned lamellae are contained within dendrites previously identified as monocrystals [1]. The spacing of the lamellae has been suggested [10-12] to be narrower the greater the growth rate and the shorter the dendrite initiation time. In this present communication efforts to identify any twin planes found were restricted to that possible from X-ray diffraction patterns.

In a previous investigation by one of the authors [2], electrodeposited zinc dendrites were identified as single crystals by both electron diffraction and polarized light extinction. However, since the dendrites obtained were not of the usual fern-like morphology (see for example [1]), and since the dendritic morphology changes with changing growth conditions, a re-examination of these dendrites as a function of their growth conditions was initiated.

2. Experimental

The potentiostatic technique used to prepare the zinc dendrites studied here was one of electrode potential, rather than current, control, i.e. the potentiostatic method. The usual 3-electrode cell [2, 13] constructed of glass was employed comprising a 1 mm diameter spherical zinc cathode, upon which dendrites were formed, a zinc anode and a zinc reference electrode. The electrode potential of the zinc cathode was controlled with respect to the zinc reference electrode with a Tacussel PIT-20-2x potentiostat; the controlled potential being either − 100 or − 200 mV.

The dendrites in this work were allowed to grow upon the spherical cathode in completely random directions, i.e. the growth was not constrained as it is, for example, in the growth method used by Ogburn *et al* [14].

Three different types of dendrites, classified by their growth rate, were grown and studied. These were:

(a) Slow growth rate (SGR) dendrites obtained from a solution of 10% wt/wt KOH containing 0.01 molar ZnO at − 100 mV zinc overpotential and 35°C. Growth rate 3 μm min^{-1}.

(b) Moderate growth rate (MGR) dendrites obtained from a solution of 10% wt/wt KOH + 0.1 M ZnO at − 100 mV zinc overpotential and 35°C. Growth rate 2.4 μm min^{-1}. This type is identical to that previously studied [2, 13].

(c) Fast growth rate (FGR) dendrites obtained

from a solution of 40 wt/wt KOH + 0.2 M ZnO at − 200 mV zinc overpotential and 35°C. Growth rate 67 μm min^{-1}. These types of dendrites are identical to those studied kinetically by Mansfield and Gilman [15] and Naybour [16].

Following growth, each dendrite was isolated and subjected to examination by X-ray diffraction and scanning electron microscopy. For the X-ray diffraction studies the dendrite was mounted on a glass fibre so that the central spine of the dendrite was parallel to the glass fibre axis. The dendrite was then placed in a Charles Supper Weissenberg camera and oscillation, rotation and Weissenberg patterns obtained using Cu-$K\alpha$ X-radiation. For the morphological studies, the dendrites were examined directly employing a JEOLCO JSM-2 scanning electron microscope operated at an accelerating voltage of 25 kV.

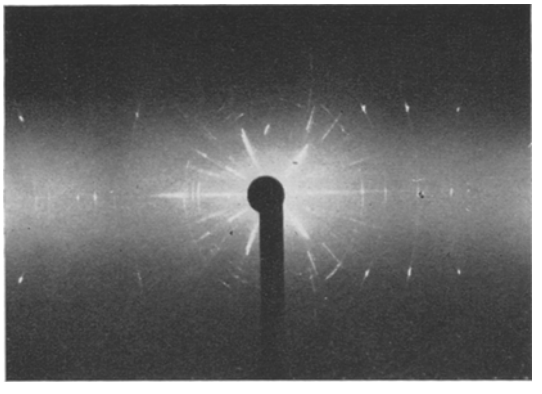


Figure 2 Oscillation X-ray diffraction pattern shown by an SGR dendrite.

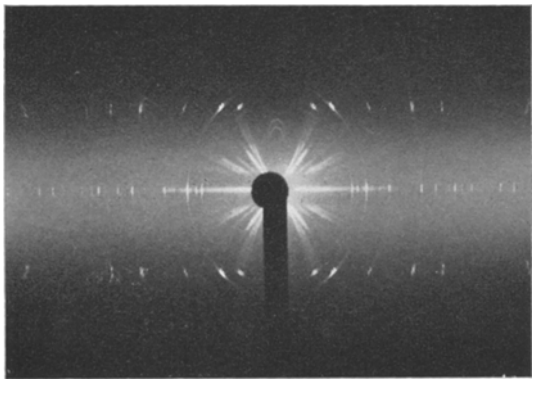


Figure 3 Rotation X-ray diffraction pattern shown by an SGR dendrite.

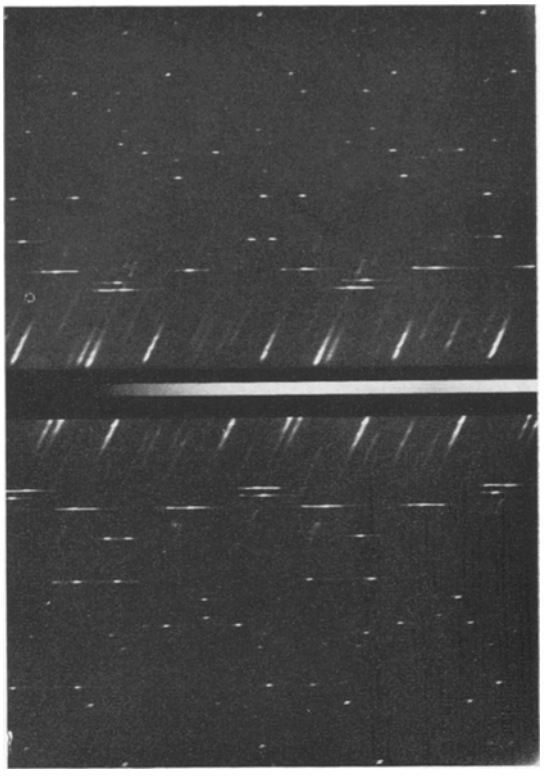


Figure 4 Zero layer Weissenberg X-ray diffraction pattern shown by an SGR dendrite.

3. Results

3.1. SGR dendrites

The oscillation and rotation X-ray diffraction patterns shown in Figs. 2 and 3 respectively, show that this type of dendrite is basically a single crystal with some polycrystalline character. The polycrystalline character is inferred from the streaking in Figs. 2 and 3 which are the initial stages in the formation of Debye-Scherrer rings.

A zero layer Weissenberg pattern (Fig. 4) indicates the presence of twinning. The spine of the dendrite is coincident with the crystallographic *a*-axis of the hcp lattice.

Fig. 5a shows the morphological character of a SGR dendrite approximately 1 mm in total length. The absence of regular branching is to be noted. Also to be noted is the base of the dendrite which appears to have been alost am point source of growth. Regular steps appear down each side of the dendrite from the tip to the base. The stepped appearance nearer the base, however, appears buried in some further growth features (Fig. 5a), presumably arising from additional nucleation after the primary growth

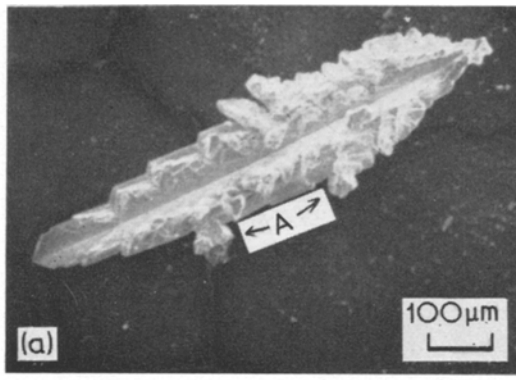
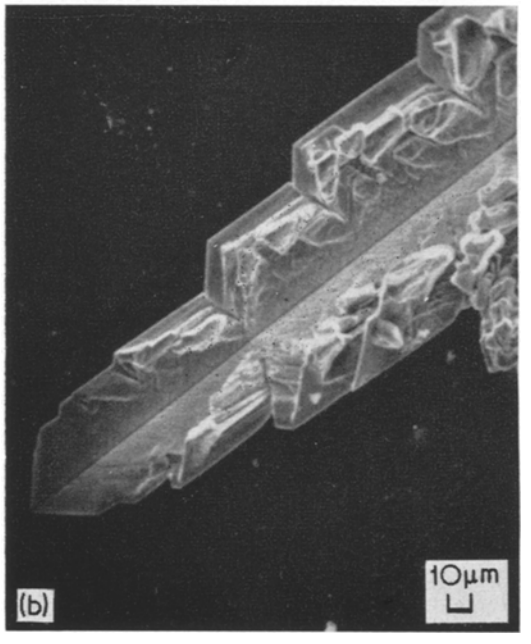
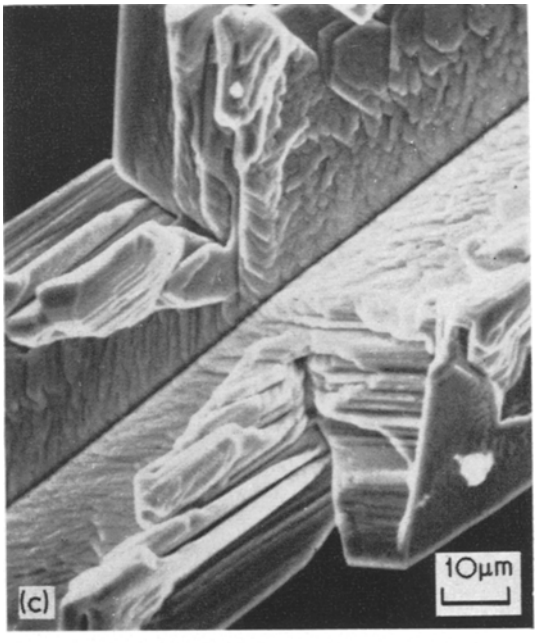


Figure 5 Typical morphology, as revealed by SEM, of an SGR dendrite.





event. It is these additional nucleated growth features (marked A in Fig. 5a) which presumably lead to the polycrystalline character observed in the X-ray diffraction patterns.

The entire dendrite can be seen to be composed of hexagonal layers. Since the dendrite spine (from X-ray data) was found to lie along the *a*-axis, the growth plane is (0001). Two layered planes, mutually inclined at 60° to each other, appear about the central spine, which is postulated as a single (0001) twin plane.

3.2. MGR dendrites

Oscillation and rotation X-ray diffraction patterns (Figs. 6 and 7) of MGR dendrites show basically single crystal patterns. However, as in the case of SGR dendrites, some streaking (elongation of the ideal single crystal spot) can be

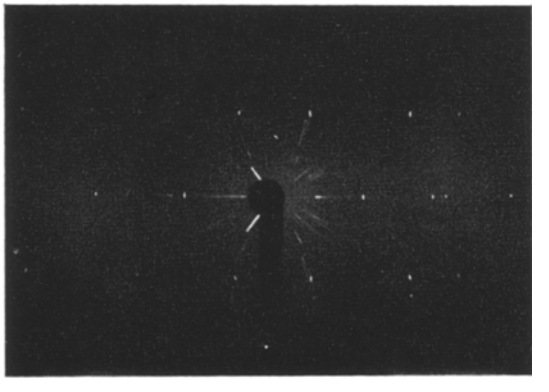


Figure 6 Oscillation X-ray diffraction pattern shown by an MGR dendrite.

observed indicating either some polycrystalline character or an ill-defined indication of the

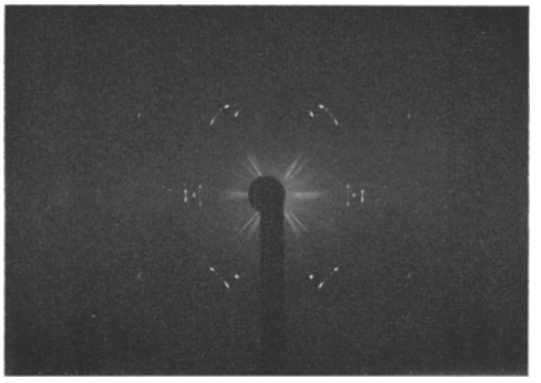


Figure 7 Rotation X-ray diffraction pattern shown by an MGR dendrite.

presence of twinning. The presence of twinning could perhaps be inferred from the morphological study (Fig. 8a); this conclusion is similar to the conclusion made by Schwuttke and Brandis [9] in their examination of silicon dendrites. The polycrystalline character (as seen by X-ray diffraction) could be produced by the presence of satellite crystals (Fig. 8b) seen upon the central body of the dendrite (as in Fig. 5a).

From X-ray diffraction, the *a*-axis of the hcp lattice was again coincident with the central spine of the dendrite.

The stepped nature of the MGR (and the SGR) dendrite is clearly seen in Fig. 8a. If this dendrite is turned over, and the upper surface examined in the area near the tip, the SEM photograph shown in Fig. 9 is obtained. The stepped nature of the dendrite is again observed, as is the angled nature of the dendrite about, what appears to be, a twin plane. That the upper surface (Fig. 9) is closer to being "atomically" smooth than the layered lower surface (Fig. 8a) is evident.

3.3. FGR dendrites

Figs. 10 and 11 are oscillation and rotation X-ray patterns of FGR dendrites. The crystallographic *a*-axis is again coincident with the central spine of the dendrite. A substantial degree of polycrystalline character, greater than that noted for either SGR and MGR dendrites can be seen in Figs. 10 and 11 as partially formed Debye-Scherrer rings. SEM studies of FGR dendrites reveals them to be distinctly different from both SGR and MGR dendrites. Fig. 12 illustrates how FGR dendrites are composed of rows of platelets stacked onto each other in a

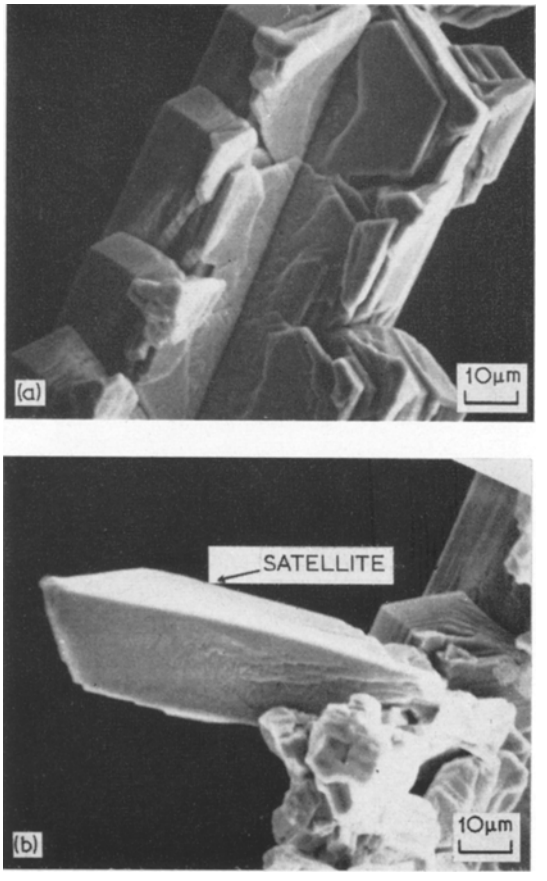


Figure 8 (a) Typical morphology, as revealed by SEM, of an MGR dendrite. (b) Example of an extraneous nucleated feature found on MGR dendrites.

"shingling" arrangement. From the shingles of a centre row, which forms the main dendrite spine, branches extend at an angle of 60°. Each branch consists again of a centre row of stacked platelets from which shingled secondary branches extend. Both the primary and secondary branches originate at the lower surface of the "parent" spine and are tilted at an angle of 60° with respect to the plane of spine (identical to the MGR dendrite shown in Fig. 9). This arrangement results in a different topography of the "upper" and "lower" surfaces, as shown in Figs. 13a and c and 13b and d.

The shingling or roof tile stacking of hexagonal platelets has been previously reported [1] for two dimensional Cd dendrites. This type of dendrite did not however produce a diffraction pattern, when the plane of the dendrite spine was irradiated with X-rays, since the plane of the dendrite deviated a few degrees from the (0001)

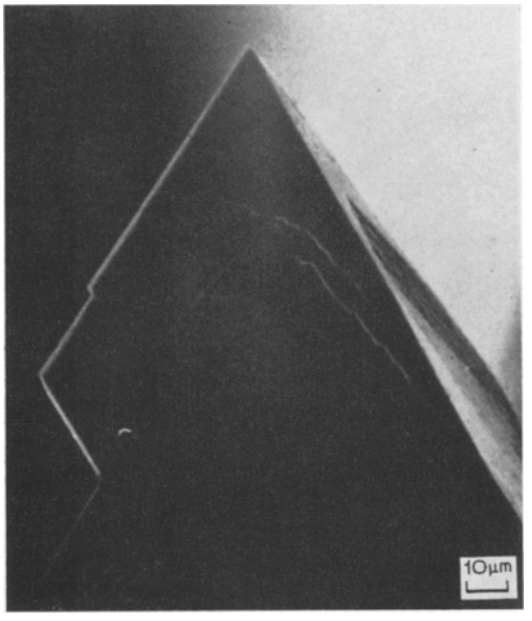


Figure 9 Appearance of an MGR dendrite when the upper surface of the MGR dendrite of Fig. 8a is viewed in the region of the tip with SEM.

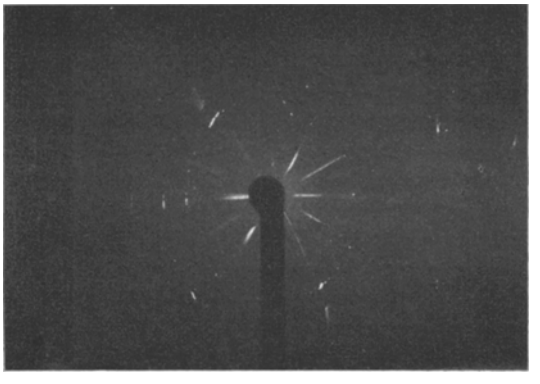


Figure 10 Oscillation X-ray diffraction pattern shown by an FGR dendrite.

plane. Wranglen [1] termed these "false" dendrites. This crystallographic data of Wranglen [1] is in contrast to the present work where the plane of the dendrite spine was identified as the hcp *a*-axis. In the present work a much greater degree of polycrystallinity is observed, compared to that observed by Wranglen [1].

4. Discussion

4.1. SGR and MGR dendrites

Both dendrites are essentially identical morphologically. From a structural standpoint both have their dendrite spines parallel to the *a*-axis with

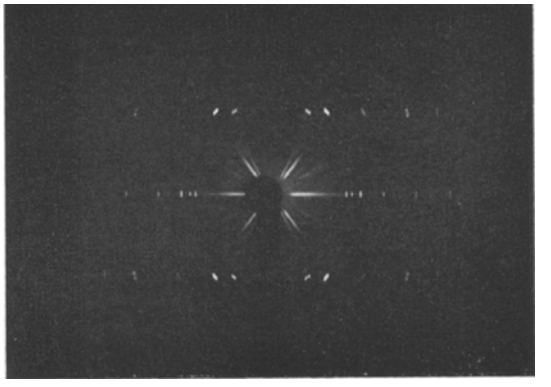


Figure 11 Rotation X-ray diffraction pattern shown by an FGR dendrite.

the growth direction being (0001). SGR dendrites are slightly more polycrystalline in nature than MGR, due perhaps to a greater number of additional nucleated features (such as the features marked A in Fig. 5a) as a result of the longer times necessary for SGR dendrites to grow to a convenient dimension (1 to 2 mm). Both dendrites are, despite the slight polycrystalline nature, seen as twinned single crystals.

The presence of twinning was observed in both SGR and MGR dendrites; in the case of MGR, twinning is concluded from SEM studies, whereas, for SGR, twinning was observed on a zero layer Weissenberg pattern.

Both dendrites are composed of layers, with the layers composing two planes mutually inclined at 60° to a common twin boundary forming a V-shaped cross section (Fig. 1). This type of morphology is similar in many respects to the so-called butterfly twins reported by DeVries [17] for barium titanate. DeVries identified an acute angle twin (38° 56′ angle between the two wings), comprising of two twin planes and an obtuse angle twin (109° 28′ between the two wings) containing a single twin plane. This single twin plane may be, in actual fact, any odd number of unresolvable twin planes as suggested by Seidensticker and Hamilton [18]. For the present SGR and MGR dendrites, the twin plane(s) can be identified as being the plane of the dendrite spine; the angle between the butterfly wings, being 60°, suggests an odd number of twin planes.

The presence of evident growth layers (Fig. 8a) on the lower surface of MGR dendrites, and the "atomically" smooth upper surface, would indicate, according to DeVries [17] that a twin

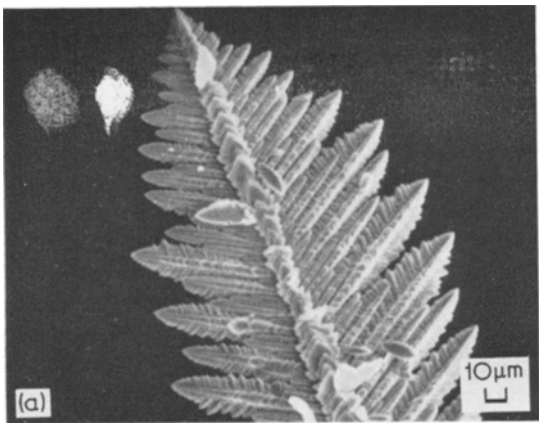
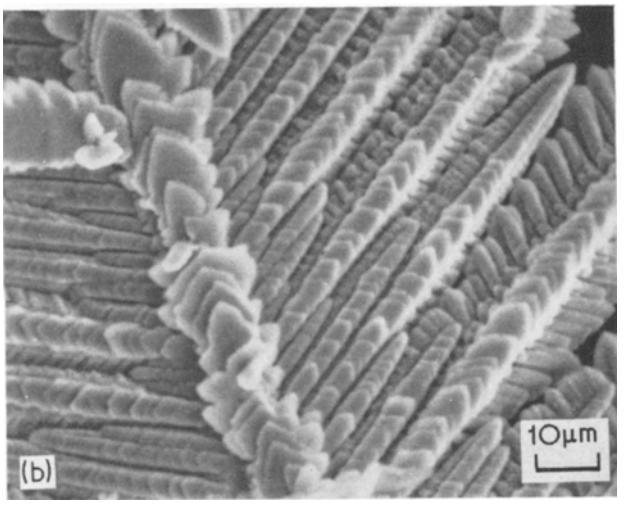
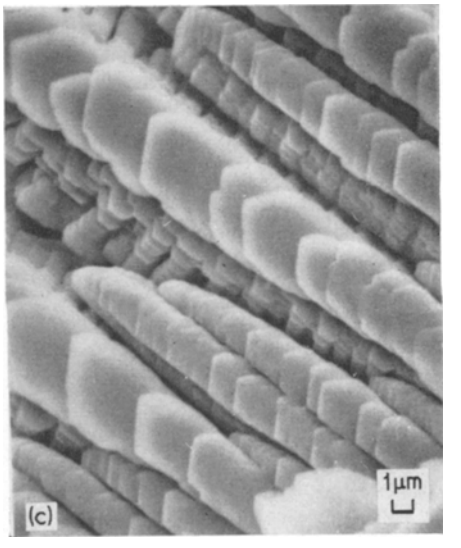


Figure 12 Typical morphology, as revealed by SEM, of an FGR dendrite.





plane re-entrant edge exists at the lower surface. From this re-entrant angle growth layers would flow to initially form the wings, and later to thicken the crystal.

In conclusion, SGR and MGR dendrites are considered essentially as examples of butterfly dendrites containing one (or any odd number) twin planes. A twin plane re-entrant edge growth mechanism is considered to be in accord with the findings reported here.

4.2. FGR dendrites

Morphologically and structurally these FGR dendrites are distinctly different from both SGR and MGR dendrites. However, as for the SGR and MGR dendrites, the spine of the FGR dendrite lies parallel to the *a*-axis with the growth direction being (0001).

The strong polycrystalline character of these zinc hcp fern-type dendrites is seemingly in contrast to the work of Wranglen [1] with Cd (hcp) fern-type dendrites which were reported as being monocrystalline with some slight crystallite misorientation. This discrepancy is considered to be due to a much greater degree of crystallite misorientation, in the present work, as compared to that of Wranglen [1]. In addition, the true degree of polycrystalline character may have been difficult to determine in the work of Wranglen [1] because of the experimental X-ray technique used. Wranglen employed a diffractometer which surveys only a limited amount of scattering space. As a result it is more difficult to detect the presence of polycrystalline character. The X-ray diffraction techniques employed here survey a much greater scattering space, and hence are more sensitive to polycrystalline character. The limitations of Wranglen's [1] technique have been previously mentioned by other authors [14]. The polycrystalline character

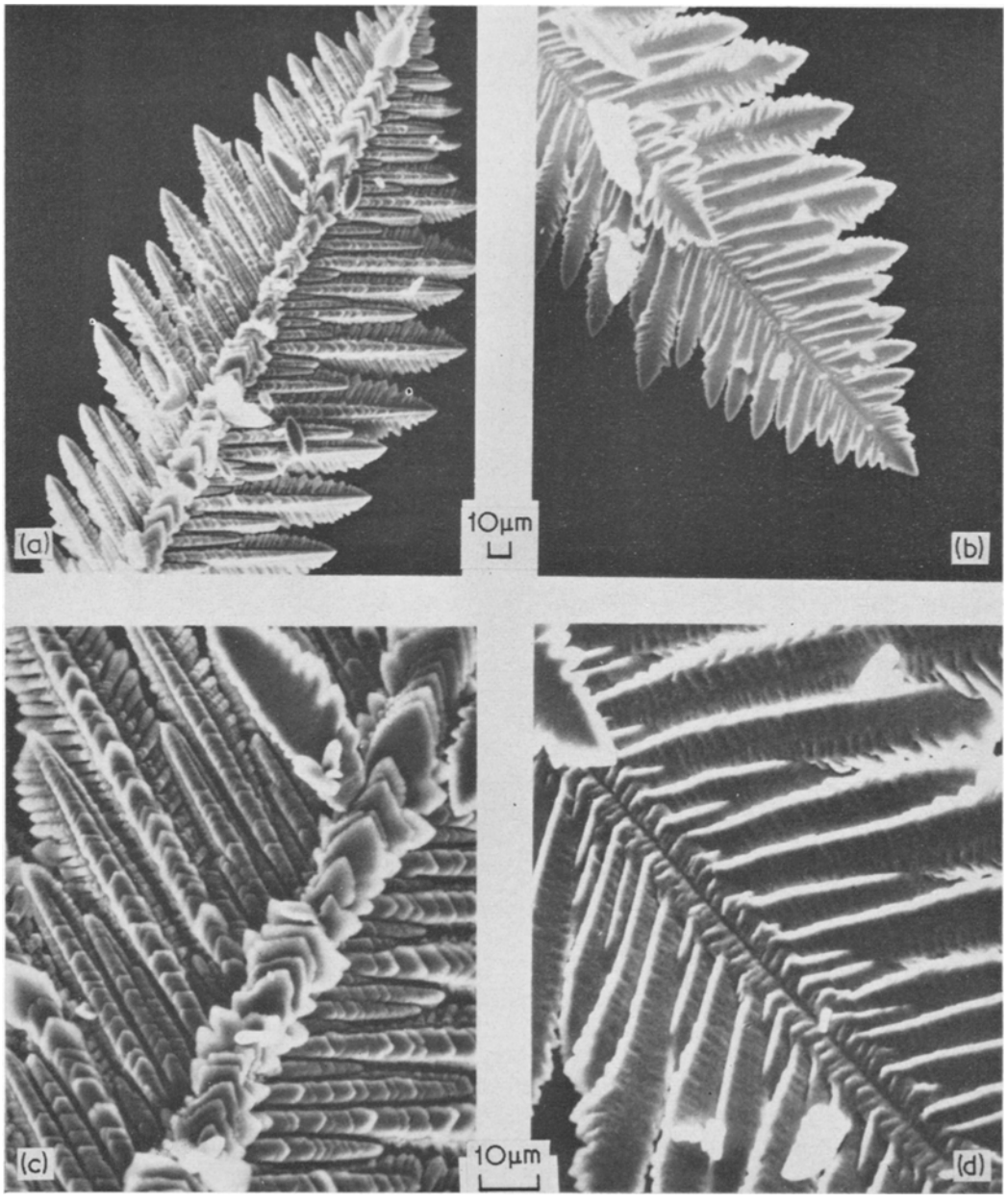


Figure 13 Upper (a and c) and lower (b and d) surfaces of an FGR dendrite as shown by SEM. The designation of upper and lower is arbitrary – lower, in the present FGR work, is assigned to the side where a dark line, possibly indicating the dendrite spine, is evident.

of the FGR dendrite is considered to arise from the fact that this type of dendrite is essentially a composite of a large number of identical single crystal units in different orientations. The single crystal unit can be identified as the platelets visible in Figs. 12 and 13 where each platelet can be said to be a very small version of the SGR dendrite shown in Fig. 5. These SGR dendrites when stacked in an angled roof-tile arrangement, as those shown as the centre spine row of Fig. 13c, show, when inverted, a groove resulting from the alignment of a large number of SGR dendrite centre spines. Thus, the FGR dendrite spine shown in Fig. 13d is not identical to the

SGR dendrite spine shown in Fig. 5.

The roof-tile stacking of SGR dendrites forms the centre row of the main dendrite, the side arms (primary branches) arise from outward growth of the stepped features of the SGR dendrite (see Fig. 5). The primary branches grow again as a row of SGR dendrites in roof-tile arrangement, from which will initiate secondary branches. Tertiary branching forms similarly.

From Fig. 13d it is clear that primary branching does not occur at each stacked SGR dendrite; this presumably being due to differing local zincate concentration and the starving of one primary branch in favour of another primary branch initiated earlier. That local zincate starvation does occur can also be concluded from the irregular length of primary branching in the same locality, Fig. 13a. Zincate starvation will, in all cases, terminate the grow and branch sequence.

Since these FGR dendrites are suggested to be composed of many SGR dendrites, the presence of twinning can be inferred, i.e. each SGR dendrite platelet is a twinned single crystal and thus the entire FGR dendrite composite will contain many twin planes. The presence of twinning will however be obscured by the extensive polycrystalline character, and thus will not be revealed in an X-ray examination.

5. Conclusions

That both structural and morphological characteristics of electrodeposited zinc dendrites are functions of the growth conditions can be concluded from the present work. However, considering the essentially identical characteristics of SGR and MGR dendrites, whose growth rates differ by a factor of eight, the growth rate may not be the only parameter of importance. That FGR dendrites, which grow approximately only three times faster than MGR dendrites, and yet are distinctly different in morphological form supports this conclusion.

Since the results of this work with respect to the growth plane, faceting plane and twin plane all being the same plane, in agreement with the requirements proposed by Faust *et al* for hcp metals, a TPRE growth mechanism would seem appropriate. However, further investigation will be needed to confirm this conclusion.

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