

Acta Cryst. (1964). 17, 774

Pseudopentagonal twins in electrodeposited copper dendrites. By F. OGBURN, B. PARETZKIN and H. S. PEISER, *National Bureau of Standards, Washington, D.C., U.S.A.*

(Received 22 October 1963 and in revised form 26 December 1963)

Dendritic growth, 'treeing', by electrodeposition was probably observed soon after Volta made his contribution to electrochemistry in 1799. Such growth occurs so readily that it has long been regarded as a problem in commercial electroplating and electrorefining. Nevertheless, electrodeposited dendrites have not received much scientific attention. The best survey of the subject is probably that of Wranglin (1955), in which dendrites of copper, silver, lead, tin, and cadmium are described in terms of the lattice geometry. Wranglin described most of the dendrites as single crystals on the basis of microscopic examination and a few X-ray diffraction photographs.

Some authors, *e.g.* Pick, Storey & Vaughan (1960), have described the production of single crystals by electrodeposition. The present authors have taken up similar studies because growth by electrodeposition under carefully controlled conditions may provide a method for production of crystals free from thermal strains. The well-known difficulties associated with growth at or slightly below the melting point may not apply. Moreover, the ease with which the rate of crystal growth can be controlled is not matched by most other techniques.

By normal procedures, growth twinning may not be a common phenomenon in face-centered cubic metals, yet it has been previously reported for instance in aluminum (Orem, 1963). However, growth twinning appears to be widespread in electrodeposits. Faust & John (1961, 1963) found twins in electrodeposited dendrites of lead, aluminum, copper and gold twin lamellae in silver dendrites growing in the $\langle 110 \rangle$ directions.

Pseudopentagonal $[110]$ whiskers of nickel, iron and platinum have been grown from vapor by Melmed & Hayward (1959) and explained as consisting of (111) twins involving five individual crystals subjected to a slight lattice strain. While essentially agreeing with this interpretation, a possible minor modification arises from the following discussion of the twin geometry.

Basically the pseudopentagonal character arises from the fact that the angle $\widehat{111\ 11\bar{1}}$ is $70^\circ 32'$ or nearly $360^\circ/5$. Since there is a twofold axis of symmetry parallel to $[110]$, most features of the twin can be described equally well or better in terms of pseudodecagonal symmetry. Fig. 1 shows the angular relationships in the $[1\bar{1}0]$ zone for the $\{111\}$ faces of a crystal *A* that is twinned by rotation about $[111]$ producing crystal *B* and about $[1\bar{1}\bar{1}]$ producing crystal *C*. Further twinning of *B* about its $[1\bar{1}\bar{1}]$ and *C* about its $[111]$ introduces only two new crystals having orientations *D* and *E*, respectively. The planes (111) of *D* and $(1\bar{1}\bar{1})$ of *E* [just as (111) indicates the position of (111) after twin operation, so $(1\bar{1}\bar{1})$ here indicates the position of (111) after two twin operations, the first of which left it unchanged] are inclined by $7^\circ 20'$ to each other, this being five times the difference between $360^\circ/5 = 72^\circ$ and the above mentioned angle $\widehat{111\ 11\bar{1}} = 70^\circ 32'$. Theoretically only three individuals are needed to show full pseudodecagonal (or pseudopentagonal) character; *A*, *B*, and *E*; or *A*, *C*, and *D*; but in practice

orientation *E* can be achieved only through orientation *C*, and *D* only through *B*; so a minimum of four individuals are really needed for this pseudosymmetry. It is easily seen how, by repeated twinning, pairs of $\{111\}$ faces at $7^\circ 20'$ to each other can be introduced all round the zone. A considerable but limited number of repetitions can produce a twin displaying clear pseudopentagonal character; but as the number of twin operations becomes large, angles that are multiples of $7^\circ 20'$ will appear till eventually the twin may resemble a polycrystalline sample with $\langle 110 \rangle$ fibre orientation.

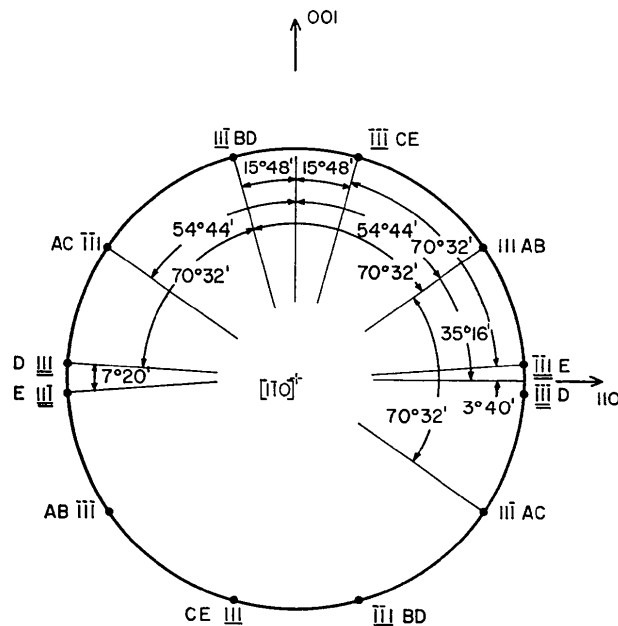


Fig. 1. Angular relationships of $\{111\}$ faces in $[110]$ zone of cubic crystals twinned repeatedly to produce pseudopentagonal symmetry along the zone axis.

A indicates original crystal.
B indicates crystal obtained by twinning *A* by $[111]$ rotation.
C indicates crystal obtained by twinning *A* by $[1\bar{1}\bar{1}]$ rotation.
D indicates crystal obtained by twinning *B* by $[1\bar{1}\bar{1}]$ rotation.
E indicates crystal obtained by twinning *C* by $[111]$ rotation.

Pseudopentagonal twins have also been observed in synthetic diamonds (Wentorf, 1963). The morphology of the diamond twins was so striking that in this instance it was possible to give convincing proof of twinning by direct photomicrography. Moreover, it is only by such clear morphological features that it is meaningful to distinguish between pseudopentagonal and pseudodecagonal symmetry parallel to a true twofold symmetry axis.

Copper $\langle 110 \rangle$ dendrites have now been grown at room temperature from a solution of 4 g.l^{-1} of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($1/64 \text{ M}$) and 0.4 g.l^{-1} of H_2SO_4 ($1/256 \text{ M}$) on a poly-