JOURNAL OF MATERIALS SCIENCE 15 (1980) 2921–2924

Crystallography of metallic aerosol precipitates

Part 2 *Solidification of droplets to spherical crystals in cadmium and zinc*

E. R. BUCKLE, K. C. POINTON*, P. TSAKIROPOULOS
Condensation Laboratory, Department of Metallurgy, The University of Sheffield, Sheffield, UK

In a previous paper it was concluded from microscopical evidence that the radius of a basal raft nucleated on a freezing droplet of Zn or Cd expands to a fixed fraction of the droplet radius before thickening into a grain. Further studies on polycrystalline spheres from condensation aerosols, together with observations by other investigators working with much larger, sessile drops, confirm that the raft remains quite thin while the radius is expanding. Additional surface features developed by epitaxial growth from the vapour on monocrystalline aerosol spheres show that in the following stage, in which the raft thickens but its upper surface no longer expands, the growth front propagates into the melt by the build-up of layers parallel to *c*. Evidence of a growth helix is found opposite the basal flat. Its formation is attributed to growth on a screw dislocation generated by the stress that accumulates at the perimeter of the expanding raft. The onset of rapid helical thickening coincides with termination of raft expansion. Differences in evaporation behaviour of particles are considered to depend on whether the dislocation remains in the solidified droplet or is expelled by thermal stresses. Glide of the same dislocations may be involved in the slip previously observed in polycrystals.

1. Introduction

In a previous paper [1] the connection between dendritic and prismatic monocrystals in Zn and Cd aerosols was shown by crystallographic reasoning. The spherical particles that also occur in these aerosols originate as droplets [2, 3], and the manner in which the droplets solidify to give monocrystals or polycrystals poses an intriguing problem. In this paper an attempt is made to explain the solidification process by combining microscopical evidence gained from the final forms of particles as seen in aerosol sediments with certain observations reported by other investigators who worked with much larger drops of the molten metals.

2. Further observations on the basal raft

Droplets of Zn and Cd condensed in the form of an aerosol appear to solidify from floating rafts that are nucleated in the liquid surface [3]. Although, in the aerosols, solidification takes place while the particles are suspended in the supporting gas, the conclusion was in part suggested by the work of Mutaftschiev and Zell [4], who reported that free-floating centres appeared and expanded to form thin, circular plates of basal orientation when sessile drops of molten Zn were allowed to cool. Similar floating entities were seen by Cahn, Hillig and Sears [5], and they estimated that the diameter was at least thirty times the thickness. White [6] found that the freezing of the upper surface of a sessile Zn drop involved the impingement of a number of facets of basal orientation. On sectioning, the facets were seen to be quite thin and to form a shell over a number of large grains extending down to the base of the drop. A closed shrinkage cavity was present at the top, between the grains and

---

*Present address: Edwards Instruments, Hampden Park, Eastbourne, East Sussex, UK

0022–2461/80/112921–04$02.40/0

the faceted shell. It was the view of White that the large grains had grown from nuclei at the bottom of the drop whereas nucleation of the facets took place independently of the substrate and at the surface of the liquid.

Apart from their larger size, the faceted drops observed by White closely resembled the multifaceted spheres of Cd and Zn described in previous papers from this laboratory (see, for example, Fig. 5c and Fig. 8 of [2]). It seems that the facets on these particles were also formed by the coalescence of thin rafts, and that Fig. 8 of [2] shows the final extent of a massive underlying grain which has grown from a point out of sight at the base of the particle. Another example is shown here (Fig. 1) in which the faceted shell has opened to disclose the shrinkage cavity. These particles were present in cloud chamber deposits but apparently solidified after deposition. In view of their size they were probably formed of liquid ejected from the super-saturator.

The importance of these observations for the solidification of aerosol droplets is two-fold. Firstly, further evidence is now provided that a basal raft has to achieve a certain radius before it can thicken into a grain. When a drop solidifies from a single raft it forms a monocrystal, and in this case it has been found [3] that the basal flat remaining on one side has a radius proportional to the drop radius. Presumably this is the radius to which the raft had grown before it began to thicken rapidly. Secondly, we now have direct evidence of the limited thickness of rafts that have not reached the maximum radius. It was not possible to see the thickness of the original raft on intact aerosol particles because the surface texture around the basal flat is continuous with that on the remainder of the grain.

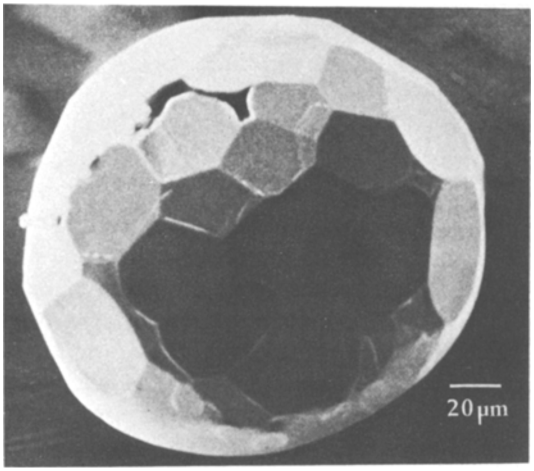

Figure 1 Multifaceted sphere (Zn).

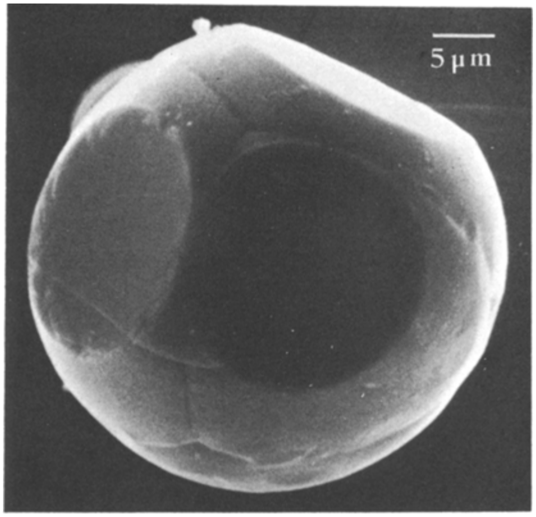

Figure 2 Spherical polycrystal (Zn) with rounded intergranular areas.

There is another feature of polycrystalline aerosol spheres which is considered to provide additional evidence of the limited thickness of a spreading raft. Full-grown rafts on the polycrystals extend inwards as grains, and narrow trenches along the grain boundaries are visible in the areas between neighbouring rafts. Usually the surface has a roughly spherical curvature in these areas (Fig. 2; see also [1], Fig. 4) but examples have occurred in which the areas containing triple-impingement boundaries are flat (Fig. 3). Other grain boundaries in such cases

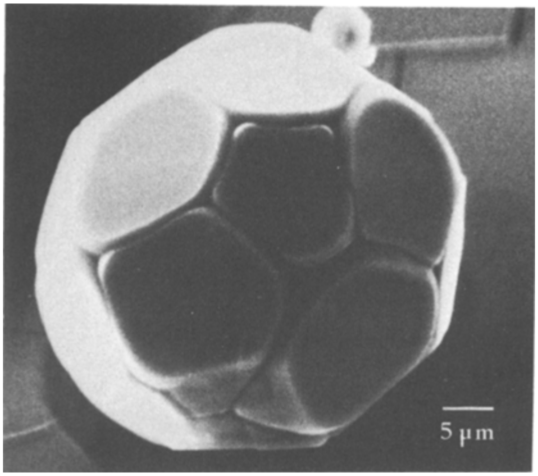

Figure 3 Spherical polycrystal (Zn) with flat intergranular area once occupied by an immature raft.

are deeply grooved, possibly as the result of evaporation. (A similar effect has been produced artificially by exposing a fall-out preparation to a flash of heat from a hot wire [7].) It is suggested that the flat intergranular regions are the sites previously occupied by immature rafts, and that these have evaporated entirely on account of their limited thickness.

3. Mechanism of formation and growth of rafts

The acceleration of growth when a raft achieves a certain radius is indicative of a change in the thickening mechanism. Addition of layers on the close-packed $\{00.1\}$ surface plane would be greatly enhanced by a switch from a mechanism dependent on two-dimensional nucleation to a helical mechanism centred on a screw dislocation which emerges on the surface. A search for evidence of growth helices in the polar region of spherical monocrystals lying opposite the basal raft has been conducted; it is this area where the front would be expected to emerge from the melt in the final stages of solidification.

In Fig. 4 the exaggerated appearance of the layer texture ("tree-rings" [2]), typical of Cd monocrystals of spherical shape condensed in a chamber at room temperature, is shown. The surface has been affected by growth in the vapour [8], so that the local detail is incidental, but epitaxy has brought out the fact that the solidification front remains parallel to and co-axial with the basal flat as it advances through the droplet. No convincing evidence of the helical nature of front propagation has been found in these preparations.

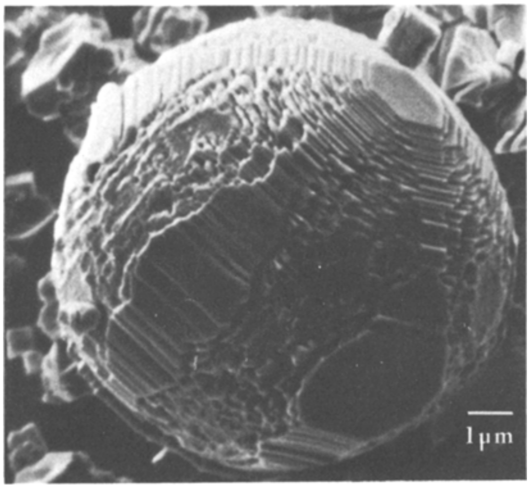

Figure 4 Spherical monocrystal (Cd) with "tree-ringed" appearance after vapour growth.

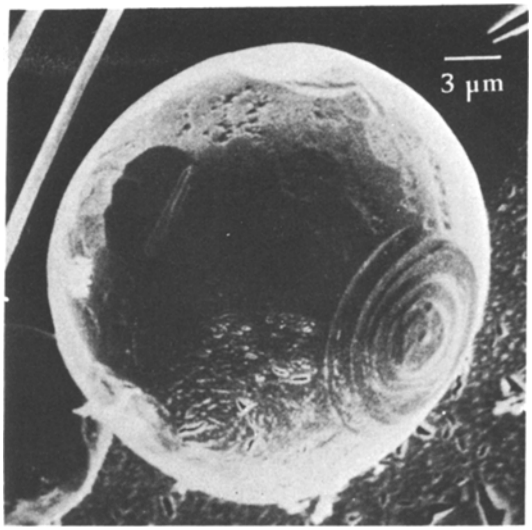

Figure 5 Growth helix on spherical monocrystal (Cd).

The smoother particles produced at higher wall-temperatures are different in that the circumferential structure relating to solidification is confined to the polar region. As previously noted [3], there occurs typically a marked groove together with a dome or hill. The hill is frequently seen to be composed of terraces converging on the pole. At the pole there is a flat area of varying extent, and in the sphere of Fig. 5, where pits are present elsewhere on the surface which indicate that evaporation has occurred following solidification, the appearance of the polar region is strongly suggestive of a growth hill in which turns of the spiral have been grossly and unevenly eroded, causing the edges to merge into high cliffs. The much larger particle of Fig. 6 (a monocrystal with an immature second raft) shows similar hill structure and, in addition, a system of fine concentric rings outside the coarse ones. A third example indicative of spiral growth activity during solidification is shown in Fig. 7. This particle was an isolated case in which the polar material had evidently been preferentially evaporated, possibly during the coating operation, to form a deep hole lined with a whorl of leaves. The structure suggests the etching-back of a growth hill composed of a number of closely-spaced, co-operating spirals.

The differences in these particles can be explained if screw dislocations are responsible for the rapid thickening of a mature raft. Taking

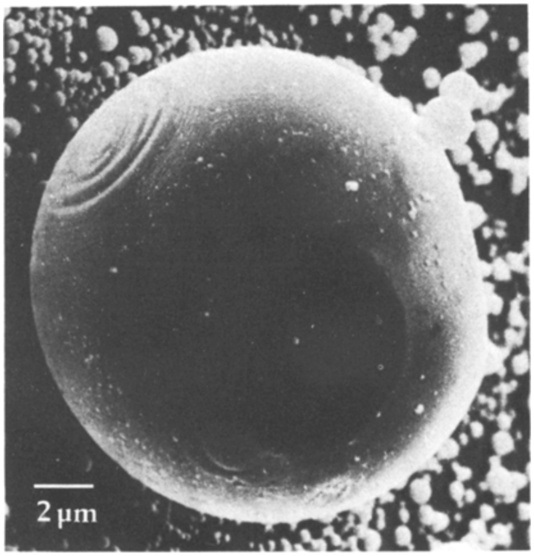

Figure 6 Sphere (Cd) with fine rings outside helix.

first Figs. 5 and 6, which represent the usual condition, evaporation at the final hill would lead to a loss of fine structure but would fail to produce a central hole if the dislocations were no longer present, having either been expelled by glide as the result of cooling stresses or, in the case of screw pairs of opposite sign, by mutual cancellation. On the other hand, the system of screws responsible for growth in the particle of Fig. 7 presumably remained locked at the axis of the crystal, providing a mechanism for spiral etching.

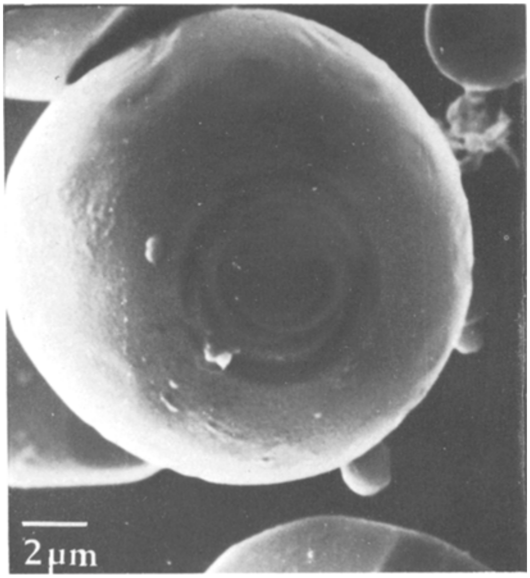

Figure 7 Sphere (Cd) with polar evaporation pit.

The overall process of solidification as now envisaged may be summarized as follows. A droplet is formed by homogeneous nucleation in the vapour, and, as it cools from the melting point, a crystal nucleus appears spontaneously on the liquid surface and spreads into a basal raft by lateral growth. The submerged basal surface is atomically flat, and its rate of advance into the melt is severely limited by the intrinsic slowness with which fresh growth layers are nucleated at the solid–liquid interface. The thinness of the raft at this stage is the result of the anisotropy of growth rate on the bounding planes [5]. At a certain raft radius, r^*, dependent on the drop radius, R, (measurements [3] gave the ratios $r^*/R = 0.53$ for Cd; 0.55 for Zn), a screw dislocation is generated on the raft axis with Burgers vector parallel to c and which relieves the stresses of surface tension building up at the perimeter. The thickening of the raft is now no longer dependent on the nucleation of layers, and growth proceeds rapidly at a self-perpetuating step as proposed by Frank [9].

The influence of thermally-induced stresses in these highly anisotropic metals was suspected as underlying the slip observed to occur spontaneously in polycrystals [3]. It is possible that glide of the dislocations formed in the rafts is involved here also, and that the observed slip actually affords indirect evidence of the presence of dislocations during solidification.

Acknowledgements

We thank the S.R.C. for supporting this work and the Bodossaki Foundation of Greece for a maintenance grant to P.T.

References

1. E. R. BUCKLE and P. TSAKIROPOULOS, *J. Mater. Sci.* 14 (1979) 1421.
2. E. R. BUCKLE and K. C. POINTON, *ibid.* 10 (1975) 365.
3. *Idem, ibid.* 12 (1977) 75.
4. B. MUTAFTSCHIEV and J. ZELL, *Surface Sci.* 12 (1968) 317.
5. J. W. CAHN, W. B. HILLIG and G. W. SEARS, *Acta Met.* 12 (1964) 1421.
6. D. W. G. WHITE, *J. Inst. Met.* 99 (1971) 287.
7. E. R. BUCKLE and P. TSAKIROPOULOS, *unpublished work.*
8. E. R. BUCKLE and K. C. POINTON, *Atmospheric Environment* 8 (1974) 1335.
9. F. C. FRANK, *Disc. Faraday Soc.* 5 (1949) 48, 67.

Received 14 April and accepted 12 May 1980.