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Condensation and crystal morphology of bismuth aerosols

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Condensation aerosols of bismuth were prepared in the heat-pulse cloud chamber at various wall temperatures by flash evaporation of metal into argon at atmospheric pressure. The particles nucleate from the vapour in the liquid state only. When prepared at low wall temperatures the droplets solidify to tapered twins with an asymmetrically sited protuberance. At wall temperatures approaching the melting point of the metal the morphology of the smaller particles is affected by thermal ageing. Complex multiple twins occur, as well as twins of simpler, rhombohedral shape. A solidification mechanism is proposed for the tapered particles, by which the freshly nucleated crystal, growing at the surface of the droplet with an emergent corner, experiences a twinning shear under the influence of fluctuating stresses imposed by the particle motion. The crystal growth rate is thereby enhanced unidirectionally, and the particle becomes elongated as a result of the volumetric expansion.

1. Introduction

The nucleation, growth and evaporation of cadmium and zinc have been reported on previously [1, 2]. In addition to the advantages of low melting point and high volatility, the anisotropic crystal properties were of considerable help in the interpretation of the particle morphology. On the basis of largely qualitative reasoning, it had been concluded that low-melting metals of low volatility should behave differently from cadmium and zinc in evaporation–condensation boundary layers [3]. Observations on lead were hampered by the lack of crystallographically recognizable features on the particles [3], but fortunately this is not the case with bismuth. Like cadmium and zinc, bismuth is low-melting. It also exhibits anisotropy along equivalent directions to those in cadmium and zinc, but differs in that it expands on freezing and is much less volatile.

2. Experimental techniques

The heat-pulse cloud chamber and operating techniques used to prepare aerosols were as described before [1]. Aerosols of bismuth were made from metal of 99.99% purity and sampled at a series of wall temperatures (T_∞) varying from ambient up to 563 K. Clean particles were obtainable only by pre-evacuating the chamber to below 0.1 mPa, followed by flushing and filling with high-purity argon (99.9999%). The working pressure was atmospheric. A coat of gold was deposited on the samples of aerosol sediment by vacuum evaporation, to protect the particles from oxidation during transfer to the scanning electron microscope.

3. Results and discussion

Extensive examination of samples revealed that the particles were more or less elongated in shape and of two kinds. The first kind were rounded, and the small ones formed at low T_∞ settings were distinctly tapered (pear-shaped). The presence of flat facets gave the tapered particles a "death's head" appearance from certain viewpoints (Fig. 1). The second kind of particle appeared as T_∞ approached the melting point (T_f, 544.5 K), and was in the form of a rounded

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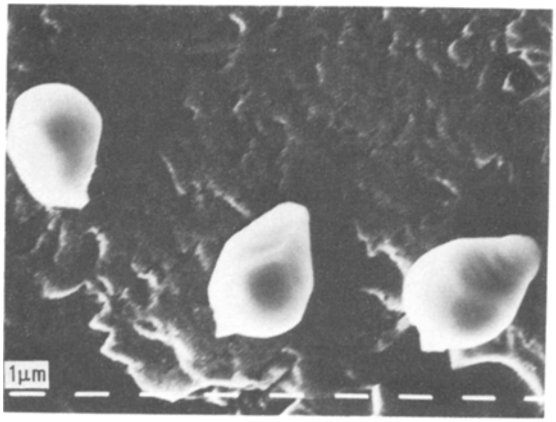

Figure 1 Pear-shaped particles.

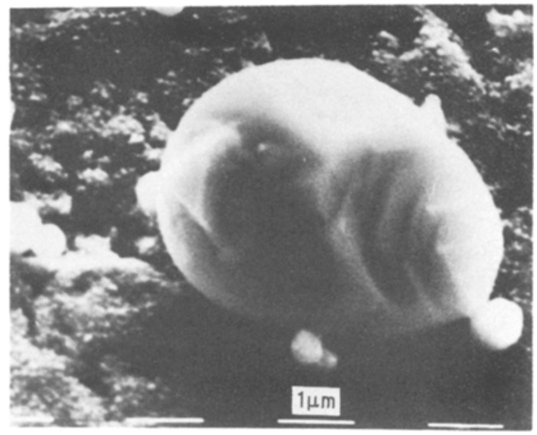

Figure 3 Truncated protuberance and terraced growth on a pear-shaped particle.

polyhedron with sharp interfacial edges between the principal faces. Isolated facets, curved in outline, were present on the residual rounded areas of the surface (Fig. 2) but tapering was slight. This particle became more polyhedral at higher at settings of T_∞. In the following the two particle types are discussed in relation to the level of T_∞ at which they were formed.

3.1. Pear-shaped particles

The smaller tapered particles, in which the death's head appearance was quite marked, varied between 2 and 10 μm across. At low T_∞, especially, they were dominated by large crystal faces of elongated and curved outline (Fig. 1). Terraces were often seen on these faces, the steps climbing in the direction of elongation (Fig. 3). The tendency was for terracing to be more pronounced at high T_∞, the smaller faces (the "eyes") also developing more clearly. A characteristic, asymmetrical feature was the presence of a protuberance. This had the shape of a trigonal pyramid, sometimes pointed and sometimes truncated (Figs. 1 and 3).

The equilibrium planes of a bismuth crystal, derived from surface energy considerations and the construction of Wolff [4] are shown in Fig. 4a. With this figure in mind, and taking account of interfacial angles measured on particles under the electron microscope, it was concluded that the crystallographic orientations are $\{02.1\}$ for the eyes and $\{10.1\}$ for the long terraced faces.

Also visible on some particles was a groove (Fig. 5), and an indentation suggestive of planes intersecting in an obtuse re-entrant angle (Fig. 6). Such an angle is known to occur in bismuth by twinning on the system $K_1 = (01.2)$, $K_2 = (0\bar{1}.1)$, $\eta_1 = [01.\bar{1}]$, $\eta_2 = [01.2]$ [5–7]. If the re-entrant angle is taken to represent this twin, the trace of the K_1 plane will coincide with the groove. Moreover, if the axis of the pyramidal process coincides with the trigonal axis, it will point at an angle of 56° to the plane K_1. The angle estimated by microscopy was close to this.

Larger particles ($> 10\,\mu$m) of the pear-shaped type occurred in small numbers at all T_∞ settings. Their shape deviated less from the spherical, due to lack of facets, but a protuberance was still present (Fig. 7). The protuberance on large particles tended to be more complicated in outline, and was frequently indented as if etched. As a rough generalization, it appeared that the protuberance is of a size constant in relation to the size of the particle.

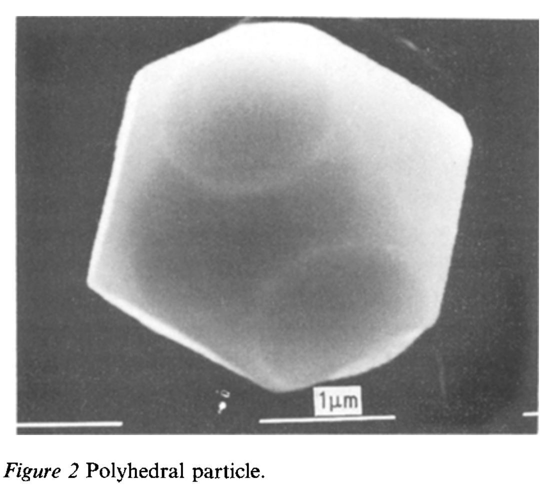

Figure 2 Polyhedral particle.

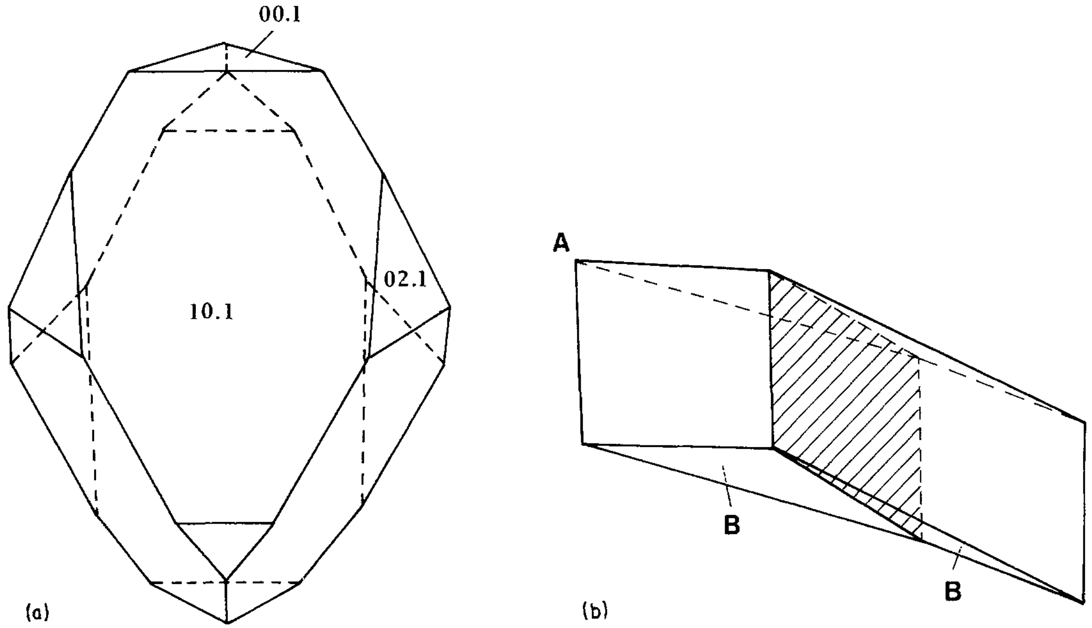

Figure 4 (a) Schematic drawing of a crystal derived from the equilibrium form and resembling a pear-shaped particle. (b) Schematic drawing of a growing twin. A: emergent corner. B, B′: $(0\bar{1}.1)_M$ and $(0\bar{1}.1)_T$ planes forming the growth front with a re-entrant angle.

3.2. Polyhedra

An increasing proportion of particles were polyhedral as T_∞ exceeded $0.8\,T_f$, although their size range was similar to that of the pear-shaped particles. Where the facets on a polyhedral particle impinged it was possible to measure interfacial angles on electron micrographs. The tendency was for the smaller polyhedra to take on simple prismatic form as T_∞ was raised closer to T_f, impingements between the facets of the equilibrium form (Fig. 4a) becoming more common (Fig. 8). The principal faces of these simple forms were deduced to be the rhombohedral planes $\{10.1\}$ and $\{02.1\}$. Typical of these particles were signs of both the groove (Fig. 9) and the re-entrant angle of the pear-shaped particle (Fig. 10). Protuberances as such were absent on the prismatic particles, but there were faint sets of rings in corresponding positions (Fig. 11). Among the largest particles formed by solidification of droplets condensed at high T_∞ there occurred complex, multiply-twinned forms of the rhombohedron (Fig. 12).

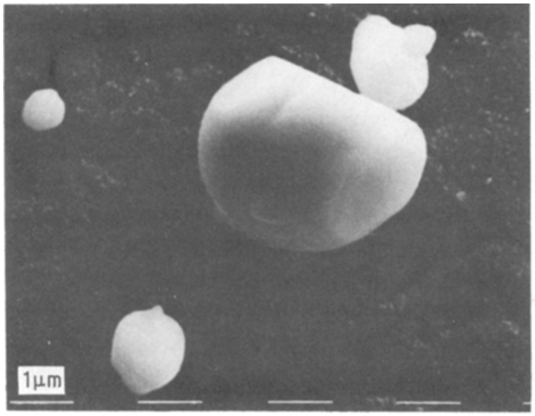

Figure 5 Pear-shaped particle showing the groove.

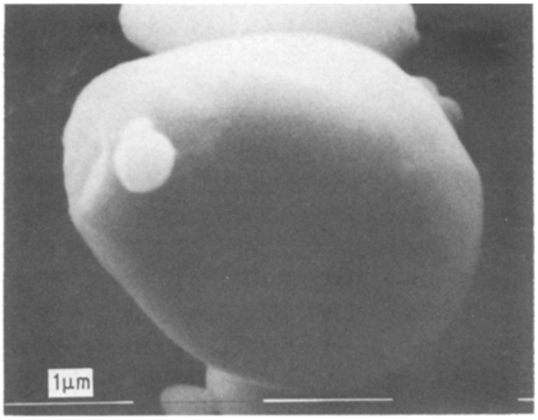

Figure 6 Pear-shaped particle showing the re-entrant angle.

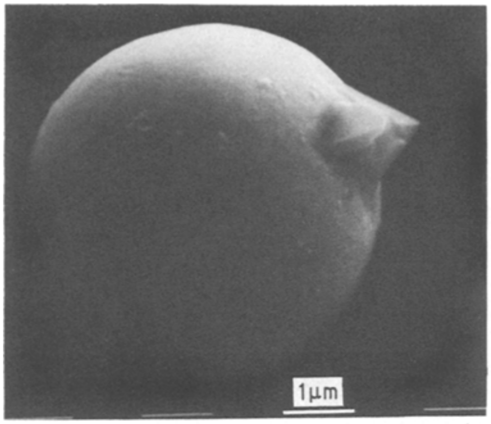

Figure 7 Large pear-shaped particle with indented protuberance and small triangular bodies.

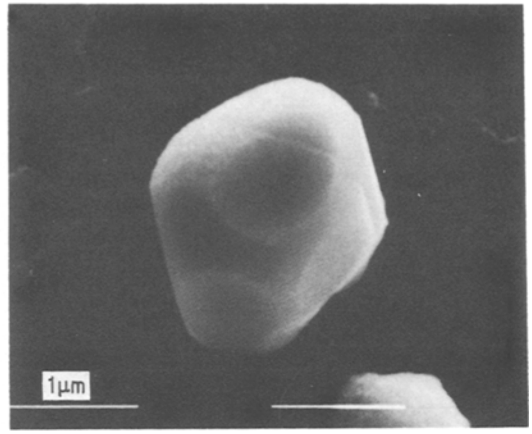

Figure 9 High-temperature particle with facets and grooves.

3.3. Mechanisms of condensation and particle growth

In general terms, the theory of boundary-layer condensation predicts that only liquid nuclei can form in the vapour of bismuth at atmospheric pressure, since, as with lead, the melting point lies below the intersections of all Amelin curves with the critical supersaturation profile [8–10]. The behaviour of bismuth at ordinary pressure is found to be in agreement with this prediction, and is also distinct from that of zinc and cadmium in that the droplets become elongated on freezing. It is to be expected that the tendency of twinned particles to elongate during solidification would be encouraged by the expansion in volume that occurs with bismuth.

3.4. The solidification mechanism

Two distinctive features associated with the early stages of solidification to a tapered and faceted crystal are the protuberance and the twin plane $K_1 = (0\,1\,.\,2)$. The absence of a projection on the smaller particles formed at high T_∞, only rings being in evidence, suggests that after solidification the shape is affected by vapour growth or surface diffusion. These processes are able to influence crystal shapes in zinc and cadmium aerosols [1, 2].

3.4.1. Role of twinning

In cadmium or zinc droplets the first steps in solidification are the nucleation and growth of a basal raft. The raft spreads over the liquid surface by a slow layer-growth mechanism, until at a critical raft radius the slow mechanism is overtaken by fast growth on a Frank helix [11]. The helix relieves the need for two-dimensional nucleation at the raft–melt interface.

The obviation of the need for interfacial

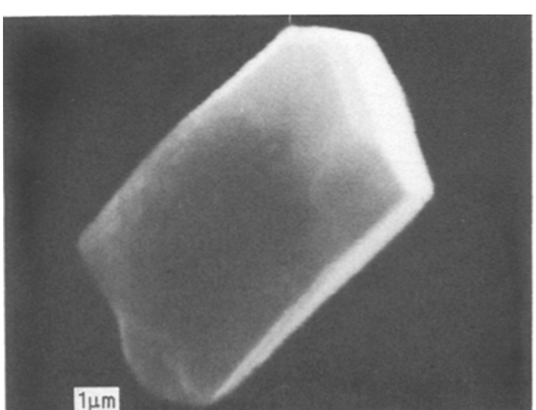

Figure 8 High-temperature prism.

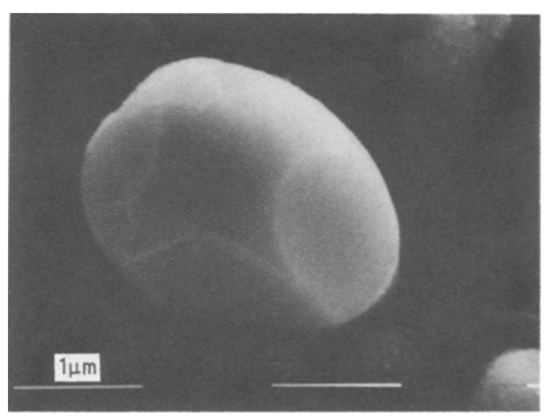

Figure 10 High-temperature particle showing re-entrant angle.

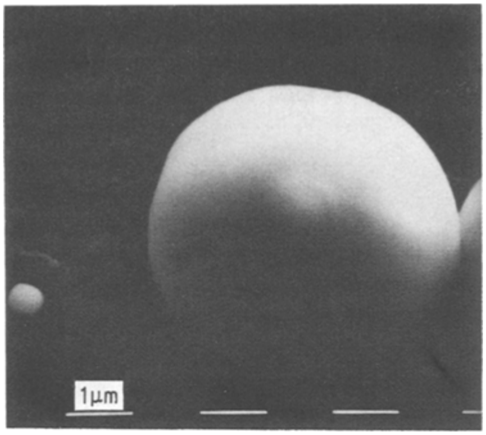

Figure 11 High-temperature particle with traces of protuberance.

nucleation in layer growth can also be achieved by twinning where this results in the presence at the growing surface of a re-entrant angle between the twin and matrix lattices [12]. It appears that, in place of the turns of a helix as external evidence of the solidification mechanism, there is with bismuth the indentation formed by the emergence of the K_2 planes from the melt (Figs. 6 and 10).

3.4.2. Nature of the protuberance

The growth of a pyramidal process on a twinned crystal in a direction almost opposite to that of solidification would seem to be an unlikely interpretation of the protuberance. It is proposed instead that the underlying explanation is to be sought in the density change, since the crystal will tend to remain at the surface of the droplet after nucleation, floating in the manner of an iceberg with a corner exposed to the gas. The trigonal shape of the corner indicates that the crystal is, in fact, a rhombohedron.

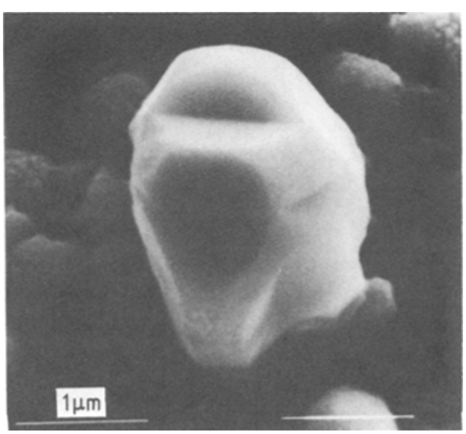

Figure 12 High-temperature multiple twin.

A crystal growing under these conditions will be subject to varying stresses, consisting of the surface tension and Archimedean thrust fluctuating with the motion of the droplet in the gas. It is possible that a twinning shear could arise from the action of these stresses to produce a crystalline particle in which the final shape depends on the size of the crystal when deformation occurred. The tapered form typical of the small particles produced at low T_∞ is, apart from the protuberance, bilaterally symmetrical, so that the plane of K_1 divides the twinned crystal into two equal halves (Fig. 4b). In the final stages of solidification the remaining melt would solidify slowly around the protuberant corner, preserving the rounded form of the original droplet. At the tapered end the melt would solidify on the $\{10.1\}$ surfaces. It is suggested that the terraces observed mark the last movements of the menisci over these faces (Fig. 3).

It is of interest to note in conclusion a number of points of contrast with zinc and cadmium. Evidence has been found, for example, of multiple twinning in bismuth but not polycrystallinity. Both successful and unsuccessful attempts at simultaneous nucleation and growth of independent crystallites in a droplet by the raft mechanism have been deduced by examination of preparations of zinc and cadmium aerosols. The only indication of second nuclei with bismuth appears to be the presence of minute triangular bodies in the frozen surfaces of large droplets (Fig. 7). The triangles could be the outlines of the protruding corners of nuclei attempting to grow near the main protuberance where the inhibiting effect of recalescence is least.

The absence of the exposed corner from the smaller particles of bismuth prepared at high T_∞ seems to be connected, like faceting, with reorganization of surface structure by thermal ageing (cf. thermal blunting [13]). This is attributable to the persistence of high levels of reduced temperature (T/T_f) following solidification at high wall temperatures. In zinc and cadmium, the mechanism of solidification is such as to preserve a spherical contour over most of the droplet, and particles retain this shape even when T_∞ is close to T_f. These metals, however, have higher melting points, and being more volatile the shape of a solidified particle is susceptible to vapour growth or evaporation [14]. The large bismuth particles retain the emergent corner and are resistant to faceting. This indicates a slowness of the growing planes of the principal nucleus to emerge on the surface of the melt. A possible reason is the failure of the stresses developed, particularly in large droplets, to reach the level required for twinning.

Acknowledgements
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