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Crystallography of metallic aerosol precipitates: dendritic origin of hexagonal prisms in Cd and Zn

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The aspect ratio was measured on simple hexagonal prisms in the sediment from condensation aerosols of Cd and Zn. For Cd the ratio $R = p\sqrt{3}/p$, where p and q are the respective lengths of the prism edges parallel and perpendicular to the basal pinacoid, varies symmetrically above and below a most frequent value of 1.2 to 1.3. The corresponding R-distribution for Zn was broader, less symmetrical and peaked at 1.5 to 1.6. Similar results had been found with hexagonal bubbles of Ar in annealed foils of these metals and interpreted as denoting the equilibrium shape. In the condensation of aerosols, however, crystals grow from the vapour under highly non-uniform conditions, and the constancy of aspect ratio is attributed to the operation of a dendritic growth mechanism as put forward by Buckle and Pointon.

1. Introduction

It was pointed out by Buckle and Pointon [1] that the upper size achieved by the monocrystalline prisms in condensation aerosols of Cd and Zn matched that of dendritic particles found alongside them under certain conditions. This observation suggested that the two types of particle have a common origin and that the prism is the perfected form of the dendrite, which precedes it and whose size predetermines the overall prism dimensions. The steep vapour pressure and temperature gradients required for dendritic growth exist only in a thin boundary layer immediately next to the hot metal source, and the prism must reach virtually its final dimensions while in this layer [2]. We now report on a study of prism sizes in aerosol precipitates which provides further support for these conclusions.

2. Experimental details

Specimens of Cd and Zn aerosol precipitates were made by the cloud chamber method of Buckle and Pointon [1, 3]. To minimize effects of residual O_2, the chamber was pumped out to a pressure of 10^{-4} Pa and flushed with Ar (99.9999% purity) three times before a condensation aerosol was prepared. The walls of the chamber were kept at room temperature and the metal in the supersaturator positioned face downwards. After coating with Au–Pd, the specimens were transferred from the cloud chamber to the scanning electron microscope (Philips PSEM 500) and measurements made of the lengths, p and q, respectively, of prism edges parallel and perpendicular to the basal pinacoid, with the object of comparing these dimensions with those of dendritic particles. Zn prisms were up to 7 μm long but Cd prisms reached only one-half this figure, and greater care as well as high magnification was necessary in making accurate measurements of Cd preparations.

To measure q for a prism, the specimen stage was adjusted to zero tilt and rotated in the horizontal plane to a position where only prismatic faces were visible on the selected prism. The error of measurement did not exceed ± 1%. To obtain p, measurement was made of the length of an edge of the prismatic plane of largest aspect (plane A of Fig. 1). The main error here is caused by the tendency of prisms to rest on a {1 0 . 0} face and, with the substrate horizontal, to present to the detector a face inclined at 30° to the vertical. Some variation in this angle could result from roughness in the substrate but the tendency is for the value of p to be too low by 13%. A smaller error, and one more difficult to estimate, arises in the lack of

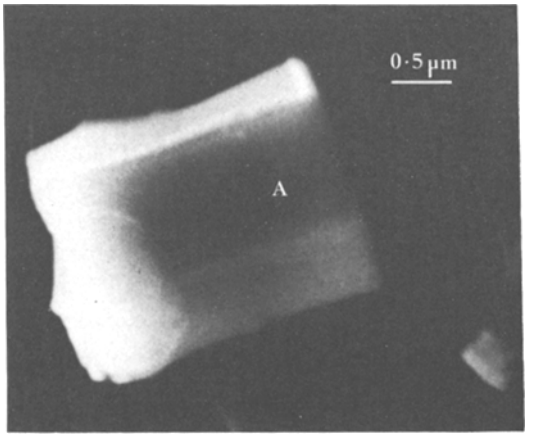


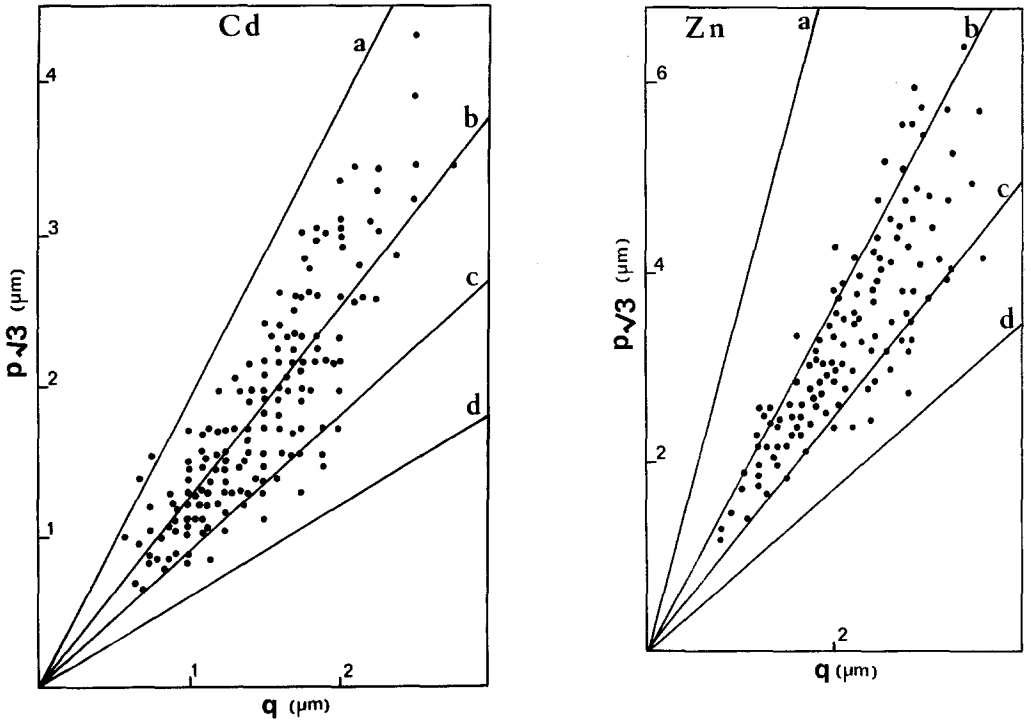
Figure 1 Zn prism positioned for measurement of q.

contrast between the adjacent prismatic faces which meet in the edge to be measured. The problem is at its worst when the stage is in position for a q-measurement, because it is then harder to distinguish the corners in which the edge terminates. About 450 prisms were measured for each metal.

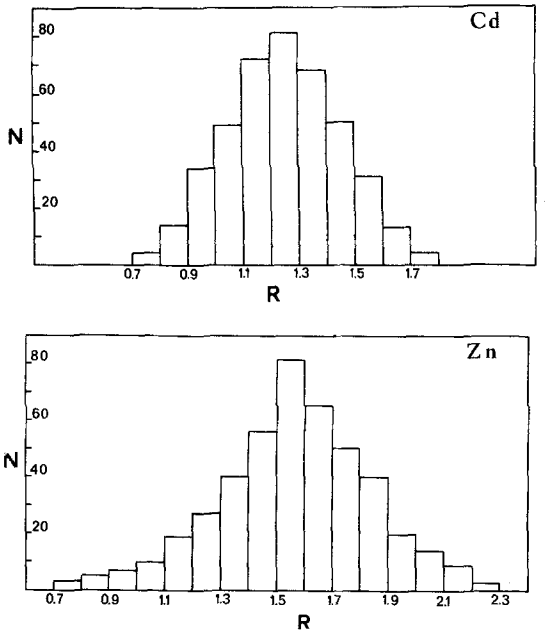
3. Results and discussion

According to the Gibbs–Wulff theorem, the ratio $R = p\sqrt{3}/q$ adopts at equilibrium a value equal to that of the ratio $\sigma_{(1\,0\,.\,0)}/\sigma_{(0\,0\,.\,1)}$ of the surface free energies of the planes which bound the crystal. In Figs. 2 and 3 are plotted $p\sqrt{3}$ versus q for the two metals, and it is evident that the ratio R is roughly constant. Distribution curves (histograms) for R are given in Figs. 4 and 5 and show the abundance N of prisms over intervals of R equal to 0.1. The most frequent value of R, which we will denote by R^*, occurs within ± 0.05 of 1.25 for Cd and within ± 0.05 of 1.55 in the case of Zn, the curve for Zn being distinctly broader and less symmetrical than the curve for Cd.

Similar distribution curves, with similar values of R^*, were reported by Miller *et al.* [4] and by Kirchner and Chadwick [5] for Ar bubbles in thin foils annealed at various temperatures after neutron irradiation, and it might be supposed that a correlation between p and q is to be expected as the result of the achievement of the equilibrium form. A distribution of prism sizes with constant R-values would be expected if the crystal nuclei took on the appropriate Wulff form at an early stage of growth. A distribution of R, on the other hand, might be attributable to variation of temperature over the surface of the source of vapour.



Figures 2 and 3 Aspect ratio of Cd and Zn prisms. Theoretical lines a to d, respectively, represent dendrite arms normal to $\{1\,1\,.\,l\}$ with $l = 2, 3, 4, 6$ (Cd) and 1, 2, 3, 4 (Zn).



Figures 4 and 5 Distribution of R for Cd and Zn.

In aerosol generation, however, particles do not grow in the early stages under uniform conditions but in a boundary layer in which are steep gradients of temperature and vapour pressure [2]. Uniform conditions are not encountered until the particles have left the layer and the growth rates have become negligibly small.

In view of this, the properties of R will be taken to indicate that a special growth mechanism is operating in the boundary layer which explains the correlation of p and q. A mechanism which does this was envisaged by Buckle and Pointon [1]. It was noticed that the prisms were matched in overall size by three-dimensional dendrites accompanying them and which, like the prisms, disappear from the aerosol to be replaced by spherical particles as the condensation conditions are changed. It was suggested that the dendrites, consisting in their most primitive condition of twelve arms radiating from a point, are the precursors of prisms, and that they, in turn, originate as solid condensation nuclei. The dendrite arms (Fig. 6) radiate in directions normal to type II pyramids, $\{1\,1\,.l>0\}$, giving the nucleus pseudo-spherical symmetry except in cases such as that shown in Fig. 7, which are comparatively rare, where nucleation twinning leads apparently to the formation of a distorted prism (Fig. 8). Growth of the dendrite arms and subsequent filling-in of the prism superstructure was thought to involve surface

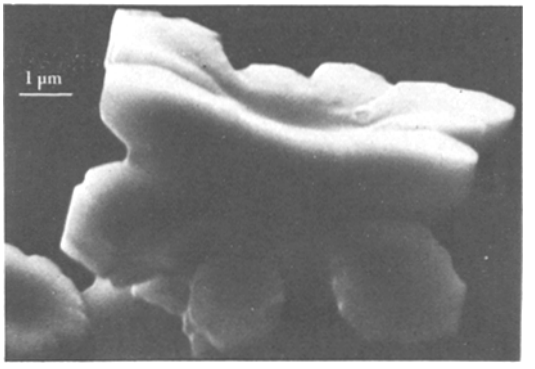


Figure 6 Zn dendrite of regular form.

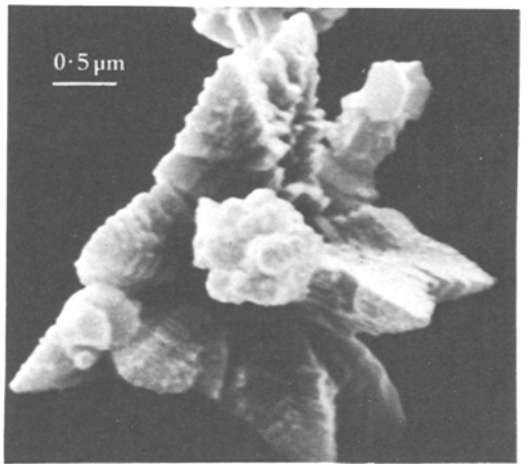


Figure 7 Twinned dendrite of Zn.

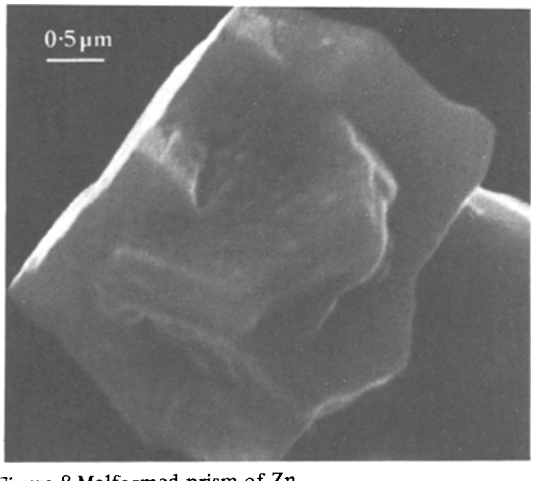


Figure 8 Malformed prism of Zn.

nucleation on terraced ledges bounded by $\{1\,0\,.\,0\}$ and $\{0\,0\,.\,1\}$ surfaces since the only evidence of dislocation-induced growth exists in the occasional c-oriented whisker projecting from the basal surfaces of full-grown prisms [1].

The present observations support this view of

the prism growth mechanism. The full lines in Figs. 2 and 3 represent R-values calculated from prisms originating in dendrites with arms pointing along the normals to pyramidal planes $\{1\,1\,.l > 0\}$. For both metals the spread of points is largely contained within the lines for $\{1\,1\,.2\}$ and $\{1\,1\,.4\}$.

The formation of pyramidal facets is not explained by the mechanism envisaged, although they have been seen on some of the prisms from aerosols condensed at higher chamber temperatures than were used in this investigation [1]. The simple prisms and the facetted prisms are similar in size, however, and it is possible that facetting occurs by evaporation after the crystals have left the boundary layer.

The width of the R-distributions cannot be explained by inaccuracies of measurement, and it is to be expected that there is some significance in the form of the curve and the peak position. Factors such as source geometry would be expected to enter here. This would affect the growth of particles over different regions of the source during the crucial dendrite stage. Extreme conditions occur at the edges of the source, where the boundary layer has gradients in more than one direction. Mis-shapen prisms such as the one shown in Fig. 8 possibly originate in such regions, and such particles were not included in the data of Figs. 2 to 5.

Acknowledgements

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