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Surface structure of spherical gamma-alumina

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Smoke produced by arcing of two aluminium rods in air is found to be composed of gamma-alumina spheres with a size range of 6 to 500 nm. While most particles are solid, single crystals with many exhibiting complicated stacking faulting and twinning, some are hollow. In appropriately clean conditions the surface is observed to be complicated, with the steps in some areas being directly related to the alumina lattice. Heating in air at 1150° C for 48 h transforms the sphere morphology of gamma to plate-and-block type alpha-alumina. Direct evidence of surface diffusion during this transformation is observed.

1. Introduction
Previous studies, based upon direct observation in bright field transmission electron microscopy (BFTEM), were largely carried out in a molecularly clean enviroment on MgO [1–3] and ZrO_2 [4]. MgO smoke, collected from burning magnesium ribbon is composed mainly of cubes, with varying numbers of plate and twinned morphologies. As a comparison with this relatively simple, structured material, the sphere morphology of alumina provides an interesting contrast.

Alumina particles of sphere morphology, prepared by a variety of methods, have been studied over the years (for example [5–7]). Spherical particles of other substances, as well as mixtures with alumina have also been studied [8–13], but in no instance have the surfaces been directly observed at high magnification and high resolution. The purpose of this preliminary study is to establish the material as gamma-alumina, demonstrate its surface character and complexity, relate that structure where possible to the lattice, and show direct evidence of surface diffusion in the transformation of the gamma spheres into alpha plate-and-block morphology.

2. Experimental procedure
A current of 15 to 20 A at 60 V was used to produce an arc in atmosphere between two $\frac{1}{8}$ in (3 mm) diameter rods of 99.99% pure aluminium. The smoke was collected at a height of $\frac{1}{8}$ in (3 mm) above the arc, directly on to a palladium 300 mesh grid. To avoid the phase–screen effect, as well as possible contamination from carbon and formvar films, which can obliterate all but the larger surface steps, no support film was utilized. To ensure a support as free as possible from contamination, grids were resistance heated to yellow heat before collection of the smoke. These as well as other criteria necessary for the direct observation of reasonably, if not molecularly, clean surfaces in BFTEM are set out by Warble [14].

The particles adhere electrostatically to the grid bars and, in spite of alumina being an insulator, mechanically stable spheres could always be found. Less instability was encountered when palladium rather than copper grids were used, a fact attributed to the absence of an oxide layer on the noble metal.

All samples were studied in a JEOL 200CX electron microscope using a LaB_6 filament, double gap condenser polepiece and top entry goniometer stage.

3. Discussion
The burning of aluminium involves an exothermic reaction. The temperature of the arc might therefore be expected not only to exceed the melting point of aluminium (660° C), but to reach the 750° C transformation point for delta-alumina. Selected area diffraction patterns showed only gamma-alumina spacings and were lacking in super-

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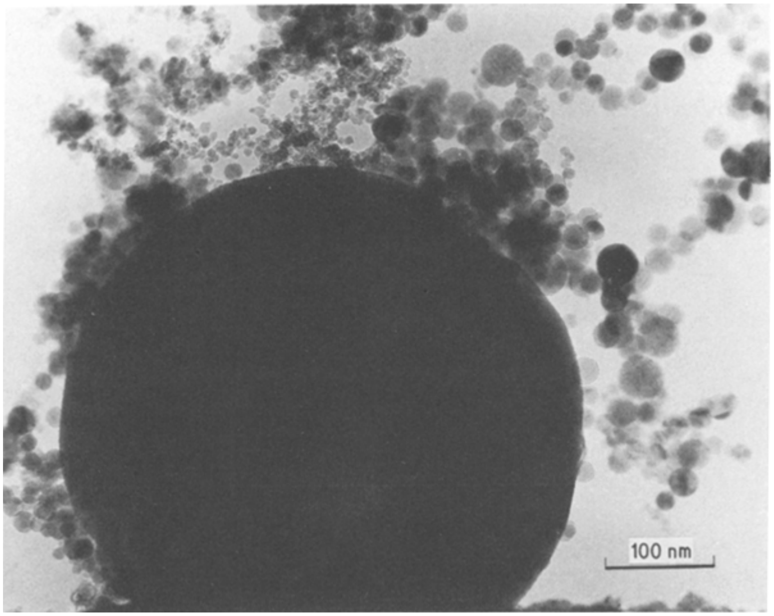

Figure 1 General field of gamma-alumina spheres showing the extremely wide size range.

lattice spacings present in the delta-phase. Furthermore, direct evidence of disorder was observed in the form of streaks in single crystal patterns, so that the phase could be positively identified as being gamma-alumina.

While Fig. 1 gives some appreciation of the very wide size range, the majority of particles tend to be in the 25 to 35 nm range. Although a large number appear relatively perfect, many show evidence of twinning (Fig. 2) and complicated faulting. Twinning can be found both through obvious shape and clear changes in the pattern of lattice images (Fig. 2). Very large particles are relatively rare, but many of those observed have been hollow.

At low magnification nearly all particles appear as smooth-surfaced, near-perfect spheres. At higher magnification, with appropriately clean surfaces, they are observed to be covered with relatively complicated patterns of steps (Fig. 3) which can be correlated with lattice planes. How the "average" sphere shape is achieved, through series of steps

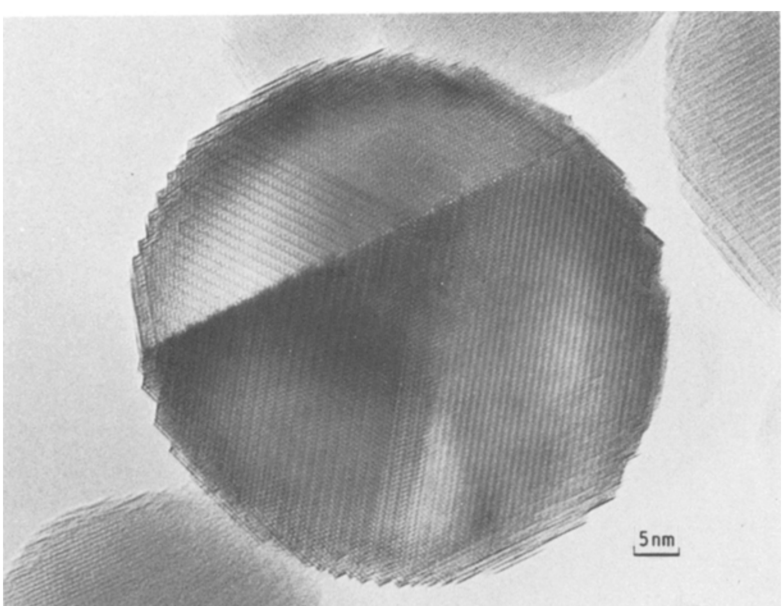

Figure 2 Enlarged sphere showing twinning, as evidenced by crystal shape as well as from the lattice imaging. The correlation of surface steps with lattice planes is clearly observed.

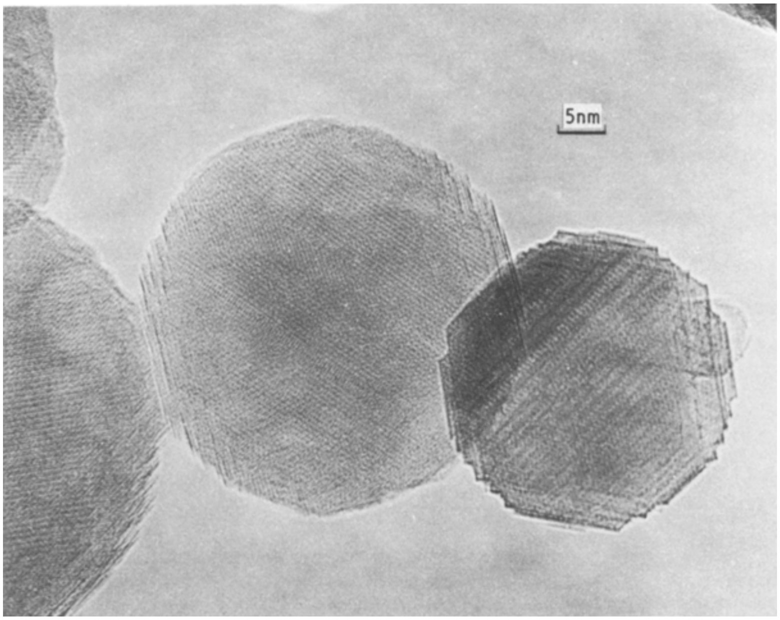

Figure 3 Imaging of the surface, as well as the lattice, under appropriately clean conditions, shows complicated step-and-lattice structure. How the material achieves an "average" sphere shape through changing step and tread lengths is directly observed.

with changing step and tread lengths, can be directly observed and is shown enlarged as in Fig. 4.

Faceting is observed occasionally and takes various forms, from faces showing contrast patterns which are just detectable to heavily faceted particles with very obvious morphologies. No crystal morphology other than that of a truncated icosahedron has been identified.

Heating the spheres at 1150° C for 48 h in air results in transformation of the gamma- to alpha-alumina plate-and-block morphology (Figs. 5 and 6). Arcs of contrast on the radiused surface are interpreted as waves of material diffusing across the surface toward alpha-alumina particles.

4. Conclusion

Arcing aluminium in air is found to produce gamma-alumina spheres with an average diameter of approximately 30 nm. Most are solid, single crystals with many exhibiting stacking faulting and twinning. Some are hollow. The surface is complicated, with steps in many areas directly related

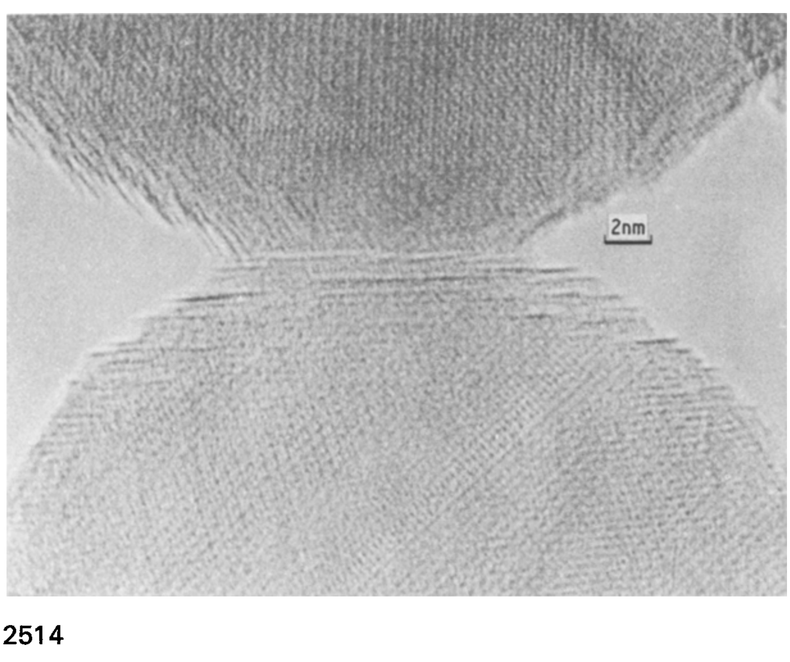

Figure 4 Enlargement of Fig. 3 showing relative relationship of step and lattice structure to intergrowth area.

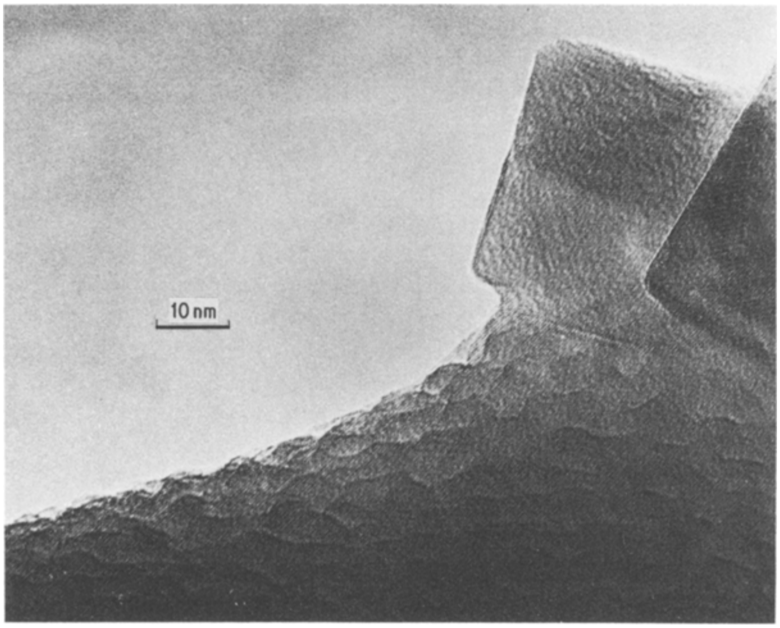

Figure 5 Gamma spheres heated in air for 48 h at 1150° C transform to the plate and block morphology of alpha-alumina (upper right).

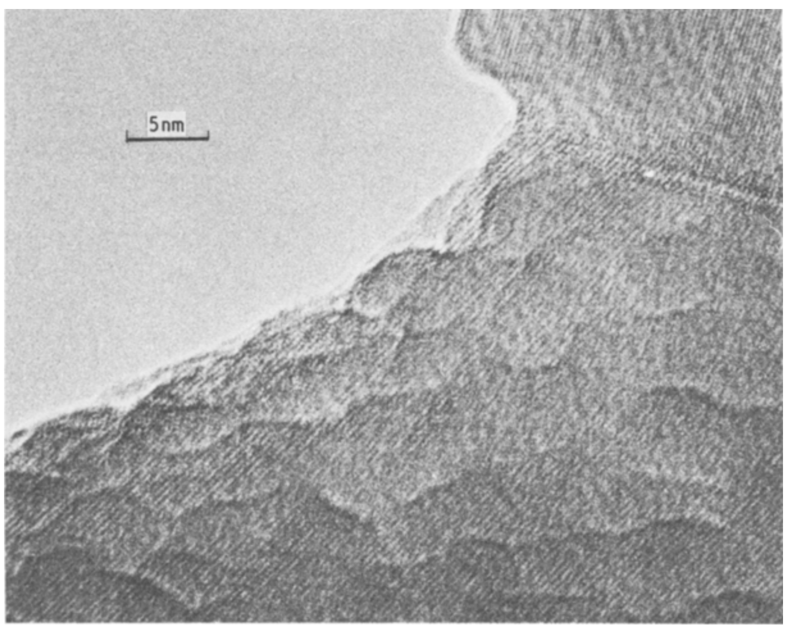

Figure 6 Enlarged section of Fig. 5 showing arcs of contrast interpreted as waves of materials diffusing over the surface toward growing alpha-alumina particles.

to the alumina lattice. Transformation of the spheres into the plate-and-block type morphology of alpha-alumina occurs when the spheres are heated at 1150° C for 48 h in air. Direct evidence of surface diffusion during this transformation is observed.

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