OURNAL OF MATERIALS SCIENCE 9 (1974) 1999–2006

The growth of highly perfect alumina platelets and other oxides by solvent vapour transport

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Very thin, highly perfect crystals of α-alumina of dimensions 0.5 to 10 μm with areas up to 5 cm^2 have been obtained by transport of alumina in the vapour phase during the evaporation of solutions of alumina in lead fluoride. The crystals always contain at least one twin plane and appear to be a unique form. Surfaces are typically free from macroscopic growth steps and no dislocations have been detected by etching or electron microscopy.

It is proposed that alumina transports via a gaseous complex and some evidence for growth of a VLS mechanism is presented. The presence of condensed lead compounds on the major (0001) surfaces evidently suppresses growth along the *c*-axis. Alumina transported by other vapour solvents tends to grow as a distinct bi-pyramidal form.

The transport of oxides in other solvent/solute systems has been investigated. While many systems show evidence of vapour phase transport the crystal products are small and the transport process inefficient compared with that of the Al_2O_3–PbF_2 system.

1. Introduction

Various vapour transport processes have been studied for the growth of alumina crystals, both as bulk crystals and dendritic platelets, e.g. by hydrolysis of $AlCl_3$ vapour. Generally the crystal quality of such platelets is poor and surfaces are stepped and irregular.

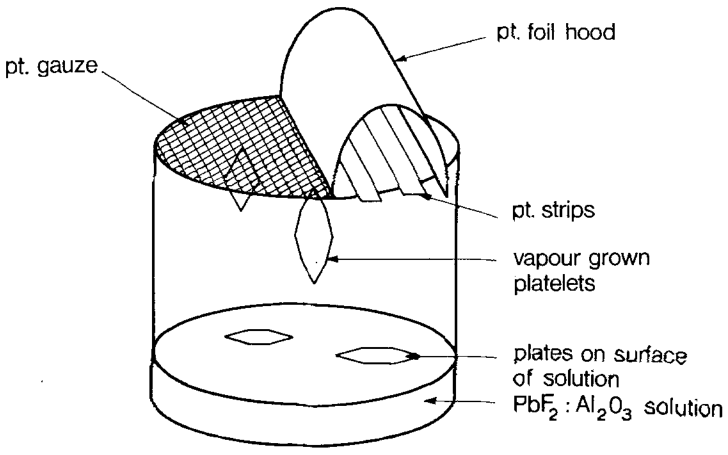
The vapour transport process first described by Timofeeva [1] and Butcher and White [2] has been modified to produce large, highly perfect alumina crystals of extreme aspect ratio (surface area:thickness). These crystals offer advantages for use as substrates for epitaxial deposition because of their surface perfection and uniformity of thickness, and for cell "windows" used in high voltage electron microscope studies.

The process is tentatively called "solvent vapour transport" since it has only been successful in transporting alumina and other oxides by evaporation of solutions in relatively high density solvents.

This paper deals with the attempt to make the transport process controllable for reproducible growth of crystal batches and also reports on the study of crystal morphology and perfection and possible transport mechanisms.

2. Experimental

Transport occurs when a solution of Al_2O_3 in PbF_2 is allowed to evaporate freely in the range 1260 to 1380°C, i.e. near or above the boiling point of PbF_2 at 1293°C. Because of the corrosive nature of the solvent, platinum apparatus must be employed. Two sizes of platinum crucible were used: 125 and 500 ml, the latter yielding the largest platelets. Foil, bent in the form of a hood, was used to modify the vapour flow, while platinum strips and gauze were located to provide surfaces from which the largest platelets could nucleate and grow freely into the vapour flow (Fig. 1), and be easily recovered at the end of a run. For the 125 ml crucible the charge employed was 30 g of free-flowing, alumina powder (H. Djevahirdjian, Switzerland) and 150 g of high purity lead fluoride (Associated Lead Manufacturers Ltd); the fine alumina powder aided quick solution. The exact composition of the starting mixture was not critical though it was found preferable to use a ratio giving a nearly saturated solution at 1300°C, using solubility data of White and Brightwell [3]. The loaded crucible was positioned centrally in a simple refractory brick furnace heated by



PT CRUCIBLE ARRANGEMENT

Figure 1 Arrangement of baffle strip and gauze for nucleation of alumina platelet crystals.

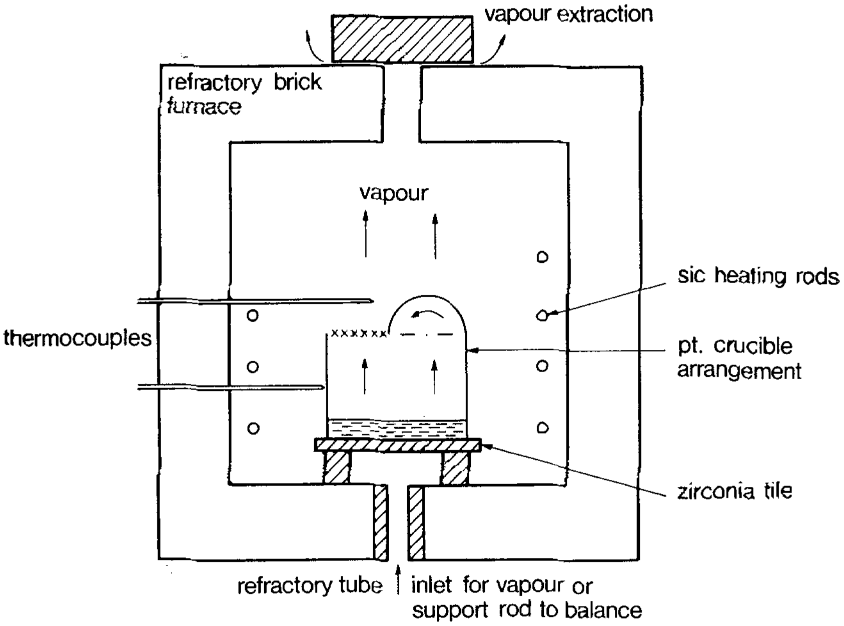


Figure 2 Furnace details for vapour transport growth.

crusilite elements, below a venting hole through which the toxic vapour could be extracted (Fig. 2). A facility for weighing to monitor the evaporation rate was included [4]. The furnace took about 2½ h to reach the growth temperature at the maximum heating rate, after which a Eurotherm PID/SCR controller maintained the set level. After a growth period of 2 to 3 h, when most of the PbF_2 evaporated, the furnace was switched off and allowed to cool before removal to inspect the products. Evaporation could proceed until almost all the PbF_2 was removed from solution; however, due to hydrolysis with water vapour, a proportion of PbF_2 was converted to PbO which could condense as droplets on the grown platelets, leading to attack of the surfaces. Thus short growth periods were preferable and the total run durations were approximately 10 h, including time for cooling to room temperature.

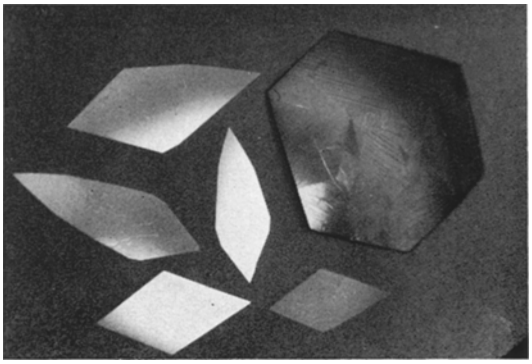


Figure 3 Vapour grown sapphire platelets compared with a solution-grown crystal (× 1).

As the vapour becomes diluted and enters the relatively cooler regions near the top of the crucible, precipitation of Al_2O_3 can occur on nearby surfaces as small three-dimensional nuclei. For reasons to be discussed later, a proportion of these nuclei can develop into platelets if they contain a favourably oriented twin plane.

Crystal formation occurs also on surfaces not in physical contact with the crucible; thus transport does not occur by solution "creeping" up the crucible walls, but entirely in the gas phase. The best yields and largest crystals were obtained at temperatures in excess of 1300° C.

Thick irregular platy crystals also form on the melt surface and crucible walls due to the solution becoming supersaturated since the relative concentration of Al_2O_3 in the gas phase is much less than that of a saturated solution. The habit and perfection of these residual crystals was quite different from the vapour grown platelets [5], as shown in Fig. 3.

Epitaxial growth on corundum seeds was also achieved and doping was possible by the addition of $\sim$ 1 mol % Cr_2O_3 to the starting mixture. Owing to the thinness of the plates, the typical pink colouration was mainly evident at the edge of thicker crystals. Experiments were carried out with other high density solvents; also with other oxides and oxide solid solutions in place of Al_2O_3. The results are summarized in Table I.

In general, although transport was observed in many systems, only tiny crystals or polycrystalline deposits resulted, apart from Cr_2O_3/PbF_2 when small plates occasionally grew. The requirements for successful solvent vapour transport are given in Table II. It would appear that the crystal products from the system Al_2O_3/PbF_2 are unique for the reasons given below.

TABLE I Solvent vapour transport systems

Solute oxide	Solvent transport agent	Crystal product
Al_2O_3 (Cr^{3+})	PbF_2, BiF_3, PbO	corundum platelets
Al_2O_3	MoO_3	corundum bipyramids
Cr_2O_3	PbF_2	plates, 3D crystals
Fe_2O_3	PbF_2	rhomboids
TiO_2	PbF_2	prisms
SnO_2	PbF_2	needles
MgO	PbF_2	cubes
ZnO	PbF_2	plates
$MgAl_2O_4$	PbF_2	octahedra
V_2O_5	PbF_2	p.c.
$Fe_2O_3 . B_2O_3$	MoO_3	p.c.
Ga_2O_3	PbF_2	p.c.
In_2O_3	MoO_3	p.c.
NiO	PbF_2	p.c.
ZrO_2	PbF_2	p.c.
also	also	
Y_2O_3, CuO, Mn_2O_3	WO_3, $PbCl_2$, BaF_2	no evidence of transport
CoO, GeO_2, $AnAl_2O_4$	BiF_3, KI	

p.c. = polycrystalline products on Pt gauze.

TABLE II Requirements for solvent vapour transport of oxides

1. Solvent metal ion of high atomic weight.
2. Oxide or fluoride anion.
3. Relatively high solubility in solution of transporting species.
4. Solvent melting point (and boiling point) in convenient range, e.g. 800 to 1400° C.
5. High solvent volatility within this range.
6. No stable compound formed between solvent and solute unless also volatile within same range.

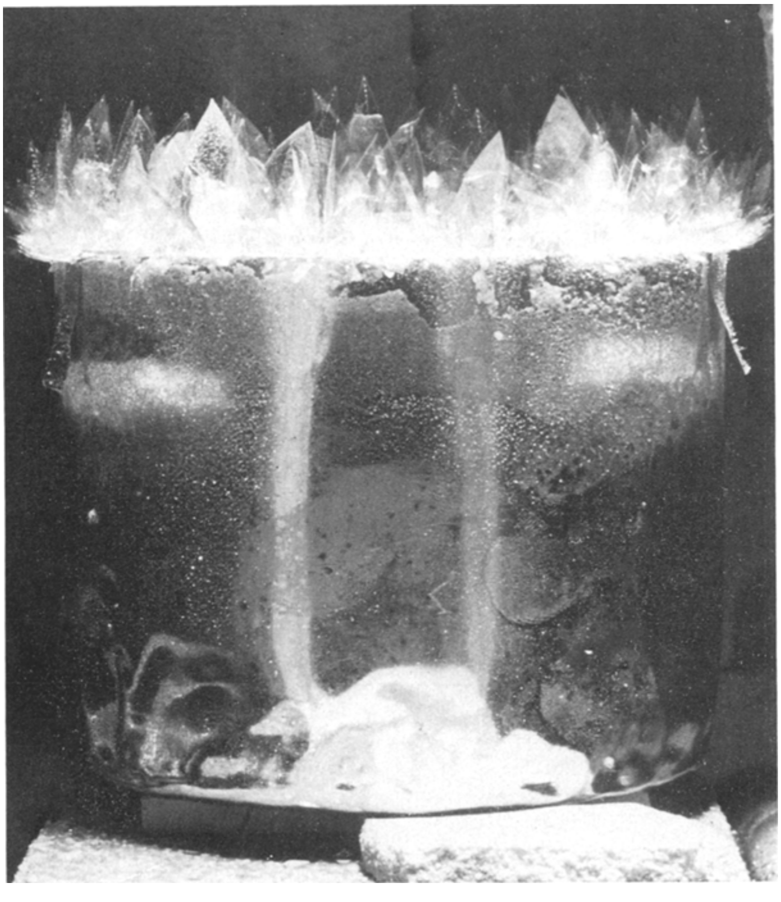


Figure 4 Products of vapour transport in 500 ml platinum crucible.

3. Crystal products

The alumina platelets always developed with the basal plane (0001) as the major surface. In the most successful runs in the large crucible 200 to 300 crystals could form, the majority of area < 1 cm^2 though often about 10% would be in the range 1 to 2 cm^2; typical thicknesses would vary between 1 to 10 μm. Fig. 4 is a photograph of the result of a run in a 500 ml crucible with the Pt hood omitted, illustrating characteristic products. Decoration patterns of condensed PbO droplets are clearly visible on many of the platelets.

In exceptional runs areas up to 6 cm^2 were obtained in the largest specimens corresponding to an extreme length:thickness ratio of 50 000:1. At the other end of the range much thinner specimens were occasionally produced (down to 0.5 μm) exhibiting distinctive interference colours. The specimens thicker than 10 μm tended to have steps on the surfaces growing in from the edges.

Although all platelets contained one twin plane along the major axis as shown, the larger platelets were also prone to multiple twinning – an interesting example is shown in Fig. 5, in the form of a "cat's head".

4. Mode of development

The morphology of the Al_2O_3 platelets has

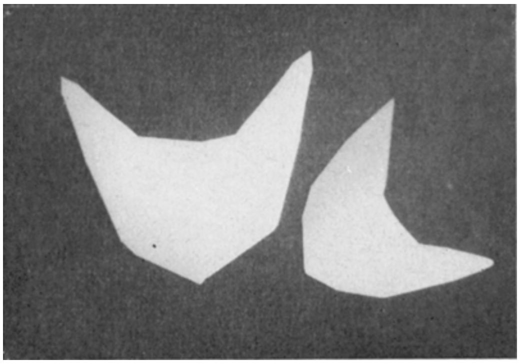
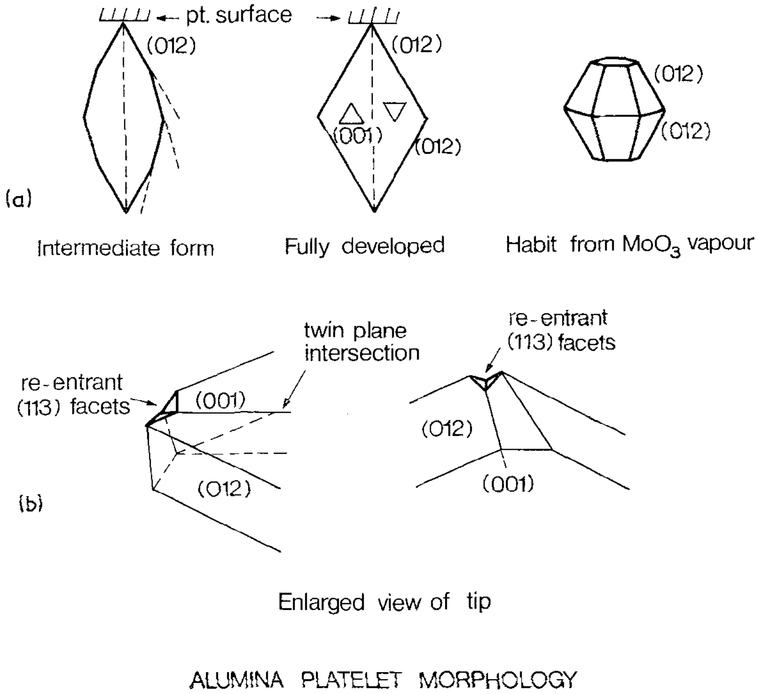


Figure 5 "Cat's-head" crystals of sapphire containing two twin planes (× 1·5).

already been described [2]; the development of the final form bounded by (012) and (001) planes appears to be via a narrower dagger-shaped form with edge facets of the type (125) (see Fig. 6a).

The abnormal morphology sometimes encountered in crystals grown by spontaneous nucleation can often be attributed to the presence of one or more twin planes. Examples of such crystals which develop abnormally with respect to either size or shape (aspect ratio) are "butterfly twins" formed by $BaTiO_3$ [6] and Ni [7], silver halides [8] and Al_2O_3 [5]. Faust and John have given rules governing the growth of crystals by



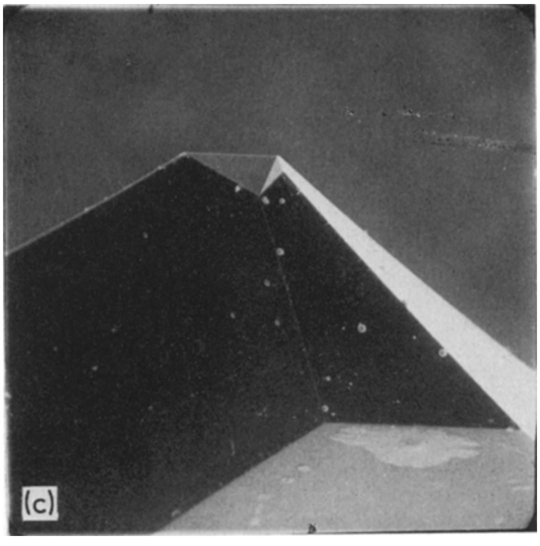


Figure 6 Details of the habit of vapour-grown sapphire crystals: (a) intermediate and final forms of platelets compared with a bipyramid grown from MoO_2 vapour; (b) details of intersection of twin plane with platelet edges; (c) scanning electron photomicrograph of twin plane termination (× 5000).

the "re-entrant twin mechanism" [9], in which the presence of two or more twin planes can act as an active nucleation centre for growth in crystals otherwise bounded by one type of habit face. For crystals bounded by two or more types of habit face, as in alumina, only a single twin plane is necessary.

Optical and scanning electron microscopy of the twin structure in the Al_2O_3 platelets revealed that at the crystal tip (opposite to the attached end during growth) a complex junction of facets was present, which included a pair of re-entrant (113) planes. It was evident that growth steps on the faces round the crystal edges originated from this intersection of (113) facets at the growing tip (Fig. 6b and c). These steps, in turn, provided nucleation sites for growth on the crystal edges fed by material diffusing from the major (0001) surfaces, which grew little in thickness during the growth cycle.

The spreading edge layers would provide vicinal faces allowing growth to occur at low supersaturations until the final (012) faces form, when growth slows down or stops unless there is an increase in supersaturation. At this stage in growth, layers could start to spread from the edges onto the major (0001) faces – thus the crystals thicken at the edges and become stepped on the surface.

The lack of growth on the (0001) faces was attributable to two factors: the surfaces were highly perfect and hence require high supersaturation levels to nucleate new layers; also there was evidence to suggest the presence of PbF_2 or PbO suppressed growth on these faces, presumably as the result of preferential adsorption of a lead-containing layer. The platy crystals grown from solution, when viewed under ultra-violet light, exhibited fluorescence which "contoured" surface growth steps. In Cr-doped Al_2O_3 crystals the edges were "buckled" (Fig. 7) which suggested trapped impurities and possibly lead compounds giving rise to a lattice mismatch, the strain being relieved by the buckling effect upon cooling. It is possible that the surfaces were covered by a thin liquid film of PbF_2 or PbO while growth occurred, analogous to a VLS mechanism. Often, striking patterns of droplets condensing from the film on the growth surfaces would result after cooling. In certain cases these droplets preferentially decorated the intersection of twin planes and other growth irregularities. Examples of this can be seen in Fig. 4, and in greater detail in Fig. 8.

Figure 7 Cr-doped sapphire plates showing edge buckling.

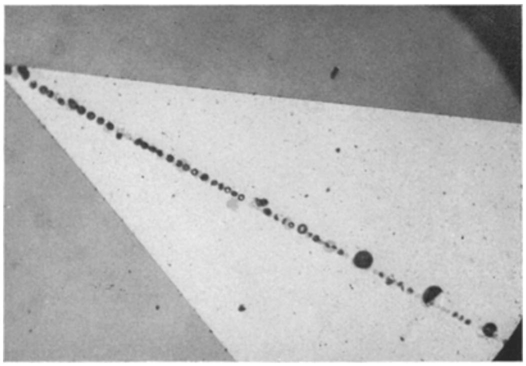


Figure 8 Decoration of twin-plane by condensed liquid droplets (× 20).

Evidence for the suppression of growth by the Pb compounds was obtained when MoO_3 replaced PbF_2 as solvent. Transport and growth were also obtained but the Al_2O_3 products were

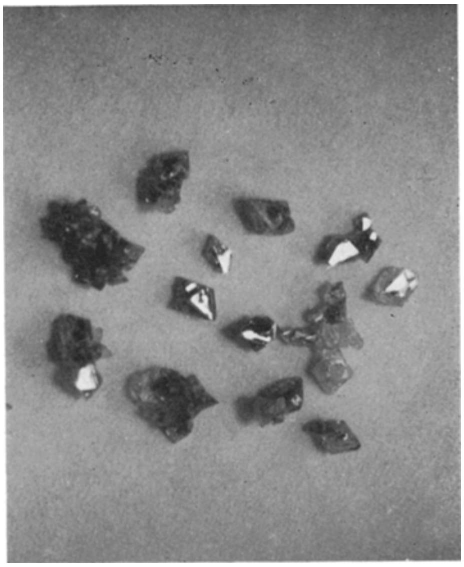


Figure 9 Sapphire bi-pyramids grown by transport in MoO_3 vapour (× 1·5).

small bi-pyramidal crystals (Fig. 9), mainly bounded by (012) faces with (001) faces absent or only vestigial. A similar comparison can be made between Al_2O_3 crystals grown from solutions in PbF_2 or Li_2MoO_4; crystals grown from the latter exhibit only small (001) facets and typically have a greater thickness:breadth ratio. Noticeably these crystals contain an appreciable amount of included Mo impurity, whereas the PbF_2 solution grown crystals contained only trace amounts of Pb.

The abnormal morphology of the platelets can thus be attributed to:

(1) the presence of a twin plane with re-entrant facets at the growth tip;

(2) suppression of growth on the basal plane by preferential adsorption of Pb compounds;

(3) apparatus geometry allowing free and unconstrained growth into the saturated vapour flow.

5. Transport mechanism

A postulated transport reaction which involves the formation of AlF_3 in the gas phase followed by oxidation reaction at the growth site [1] e.g.

$$Al_2O_{3\,(s)} + 3PbF_{2(l)} \rightarrow 3PbO_{(l)} + 2AlF_{3(v)} \quad (1)$$

followed by

$$4AlF_{3(v)} + 3O_{2(v)} \rightarrow 2Al_2O_{3(s)} + 6F_2O_{(v)} \quad (2a)$$

or

$$2AlF_{3(v)} + 3H_2O_{(v)} \rightarrow Al_2O_{3(s)} + 6HF_{(v)} \quad (2b)$$

was thought unlikely for the following reasons. Transport of Al_2O_3 was obtained using PbO only in place of PbF_2; though the process was inefficient and only small, poor quality crystals resulted, it showed that formation of an intermediate $AlF_{3(v)}$ was not necessary to the process. This was also borne out by the transport from the Al_2O_3/MoO_3 system and the fact that experiments using AlF_3 alone or AlF_3/PbF_2 systems yielded no observable transport.

Attempts were also made to modify the growth atmosphere with an inert gas, N_2, and oxygen and steam. Results were difficult to evaluate as the latter gases promoted the formation of PbO in the vapour phase which is detrimental to growth; in the case of N_2, transport was reduced but as the furnace was not airtight the result was not conclusive.

It appeared that solution of Al_2O_3 in PbF_2 was a necessary step in the process. White and Brightwell [3] showed that each Al_2O_3 molecule forms two ions in PbF_2 solvent and postulated the following reactions:

$$2PbF_2 \rightleftharpoons PbF_3^- + PbF^+$$

$$Al_2O_3 \rightleftharpoons AlO^+ + AlO_2^-,$$

followed by complex molecule formation of small concentrations of $PbAlOF_3$ or more probably $PbAlO_2F$ in the solution. The preferred mechanism in the vapour transport case would, therefore, be the formation of a volatile complex between alumina and lead fluoride, e.g.

$$n\,.\,PbF_{2(l)} + Al_2O_{3(s)} \rightleftharpoons n\,.\,PbF_2\,.\,Al_2O_{3(v)}\,. \quad (3)$$

Emmenegger has published data for other examples of volatile complex formation in the gas phase [10]. If such species have an appreciable vapour pressure at ~ 1300°C, transport can occur in the gas stream – the reverse reaction would then occur when the PbF_2 concentration decreases as the vapour leaves the crucible and expands into the surrounding region. The point at which this occurs will depend on system geometry and evaporation rate. At low rates, and with random convective flow over the melt, precipitation may occur near the liquid surface [11], but at higher rates the PbF_2 ratio would be maintained over longer distances and crystals could form on the rim or outside the crucible. Once nucleated, a proportion of these can develop into platelets tending to grow edge-on into the vapour flow – the super-saturated vapour probably condenses as a liquid on the basal planes. Larger crystals are thus promoted in laminar flow, after nucleation of small bulk crystals has occurred, as they would present larger collecting surfaces. It is interesting to note that a surface film of adsorbed PbF_2/Al_2O_3 solution would tend to evaporate from the edges due to the small radius of curvature. This would give rise to a "pumping" action; vapour species condensing on the major surfaces would flow across the surface and PbF_2 would evaporate from the sharp edges. Growth would then preferentially occur near the edges due to the increased super-saturation resulting from the loss of PbF_2.

Using the Gibbs-Thompson equation:

$$P_r = P_s \exp \frac{2\gamma M}{RT\rho r}$$

where P_r and P_s are the pressures in equilibrium with curved and flat surfaces respectively, M = molecular weight of species, r = radius of curvature, ρ = density, R = gas constant, γ = interfacial energy, and making a rough estimate of γ for PbF_2 at 1570 K as ~ 300 mJ m^{-2}, the pressure ratio P_r/P_s over the edges compared to that over the flat surfaces would be about 16:1, thus supporting the idea that surface flow is a contributory factor to the growth process.

Further work would be necessary to establish the exact nature of transporting species using transport in Pt tubes, Knudsen effusion from sealed Pt containers in conjunction with a weighing balance, and mass spectroscopy, provided the problem of the corrosive nature of PbF_2 vapour could be overcome.

6. Crystal perfection and properties

The as-grown crystals could be cleaned of condensed deposits (when no attack had occurred) by immersion in hot dilute nitric or acetic acid. Thinning could be achieved to a certain extent by controlled reaction in hot phosphoric acid.

A further unusual feature of the alumina crystals was that most were completely free of surface steps visible by optical microscopy. The structural perfection was high as evidenced by transmission electron microscopy and X-ray diffraction topography, when uniform contrast was obtained. Uniformity of thickness was shown by the constant interference colour observed in reflection in specimens up to 4 cm^2 area and 0.8 μm thickness; in general the thinner platelets exhibited a bright interference colour and grew up to ~ 1 cm^2 area.

Non-stepped platelets were quite flexible and could be bent almost double without breaking (they would be expected to have high tensile strength as a two-dimensional "whisker") unless more than one twin was present.

Selected platelets have been used for substrates for epitaxial deposition of Cr_2O_3. Although handling presented some problems due to electrostatic charging and the substrates curled after deposition of a thick epitaxial layer, presumably due to differential thermal contraction, good epitaxy was obtained on the (0001) faces.

Alumina is a desirable substrate material for certain applications because of its high thermal conductivity; the as-grown platelets provide suitable surfaces for epitaxy avoiding the need for cutting and fabrication of less perfect bulk crystals.

Acknowledgements

The authors would like to thank Mr H. B. Evans and Dr G. E. Lane for technical assistance with this project, and the Science Research Council for a contract which supported much of the work.

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Received 3 June and accepted 10 June 1974.