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Filamentary sapphire

Part 4 *Dendritic growth*

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The "edge-defined, film-fed growth" (EFG) technique was employed to grow filamentary sapphire from the melt using tungsten orifices at speeds up to 25 cm/min. Filament growth was recorded using 16 mm motion picture photography and samples grown were examined by means of transmitted light and scanning electron microscopy. Evidence for the dendritic nature of growth at speeds in excess of 10 cm/min is presented. Details of the liquid/solid growth interface are reported, indicating the increasingly dendritic character of propagation with increasing speed, and suggesting that a minimum of two related dendrites are required for stable growth. The pulsating quality of growth at high speeds is discussed in terms of a need to dissipate heat of solidification and the effect of this dissipation on the super-cooled liquid into which the dendrites extend. Other growth characteristics, including the 0.020 cm high growth film from which the 0.024 cm diameter filament is withdrawn and the defect microstructure of the solid filament are discussed.

1. Introduction

The first paper [1] in the present series described the growth and microstructural characterization of *c*-axis ($\langle 0001 \rangle$) sapphire filament. This material was grown at rates in the range 2.5 to 7.5 cm/min using a crystal growth technique called edge-defined, film-fed growth (EFG) [2-5]. Subsequent papers reported the fracture strength in tension of this filamentary sapphire [6], and the growth at rates up to 3.0 cm/min of sapphire free of the microvoids present in the earlier filament [7]. This latter filament was of sufficient optical quality to act as a light pipe.

Scanning electron microscopy examination of growth interfaces, retained by jerking 0.15 cm diameter crystals free from the melt during growth, has shown that at very fast rates growth is by means of a dendritic propagation mechanism [5]. In particular, the advancing dendrites in $\langle 0001 \rangle$ growth axis sapphire are capped by $\{10\bar{1}2\}$ rhombohedra, whose trigonal apices point in the growth direction. In the present study, 16 mm motion picture photography is used to record the changing nature of the liquid/solid interface with growth speed, and together with microscopic examination of as-grown samples, provides conclusive evidence for the dendritic character of growth in 0.025 cm diameter *c*-axis filament at rates greater than 10 cm/min.

2. Experimental

The crystal growth apparatus and growth procedures for nominally 0.025 cm diameter *c*-axis sapphire filament have been previously described [1]. The only important variation for the present study was the substitution of a tungsten growth orifice in place of the molybdenum orifice generally used. The higher thermal conductivity of tungsten at crystal growth temperatures (1.0 Watt/cm^2 °C compared with 0.4 W/cm^2 °C for molybdenum at 2000° C) has been shown to play an important role in heat transfer at the growth interface [7].

During growth, it is necessary to accompany increases in growth rate with decreases in melt temperature in order to prevent the crystal necking down and finally pulling free of the liquid meniscus film connecting it to the top surface of the tungsten orifice [1]. These mutually interacting adjustments are of particular importance at very fast growth rates when dendritic growth takes place from a substantially supercooled meniscus [5]. During the present study, these adjustments were carried out manually while simultaneously viewing the growth region through a stereo microscope. The motion picture photography was taken at 64 frames/sec, allowing a clearer description of the growth process when the film was projected at normal speed, 16 frames/sec, or slower. Samples of the sapphire grown were examined using transmission optical and scanning electron microscopy (SEM).

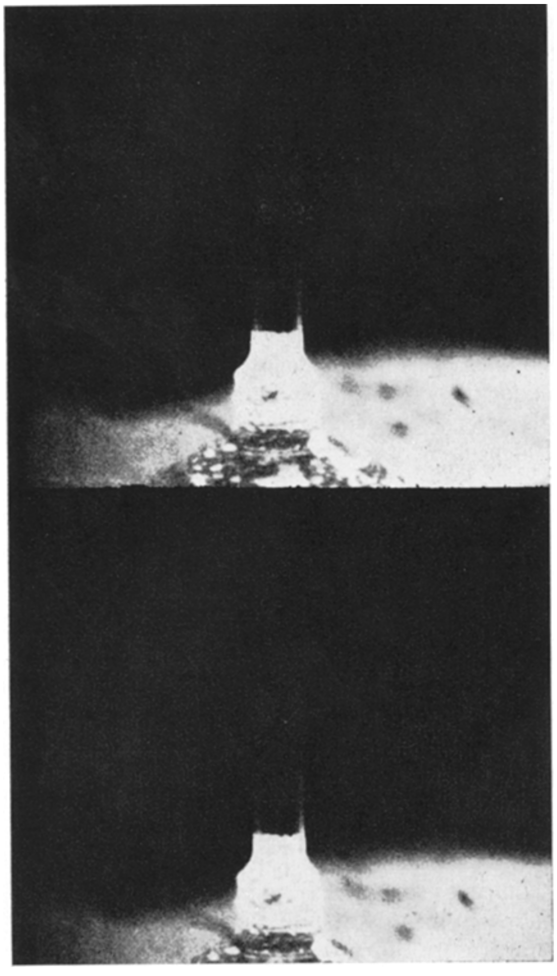

Figure 1 Motion picture sequence showing filament growth at 12 cm/min. Serrated dendritic interface is just discernible.

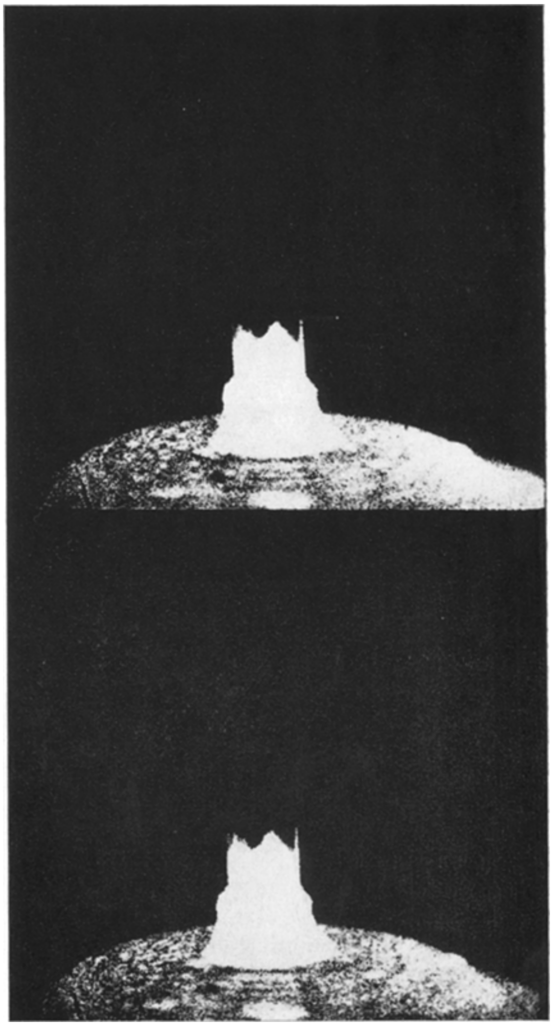

Figure 2 Motion picture sequence showing filament growth at 15 cm/min. Several dendrites are evident at the solid/liquid interface.

3. Results

3.1. Motion picture photography

Representative frames taken from 16 mm motion picture photography recording growth at rates of 12, 15 and 20 cm/min are presented in Figs. 1, 2 and 3, respectively. In Fig. 1, the dendritic nature of the interface is discernible as a series of small serrated edges ($<$ 0.001 cm long) projecting into the growth film. Surface striations, having their origin at the dendrites, run longitudinally along the filament. As the growth rate is increased to $\sim$ 15 cm/min (Fig. 2), the dendritic nature of the interface becomes increasingly evident. The number of dendrites observed at the interface

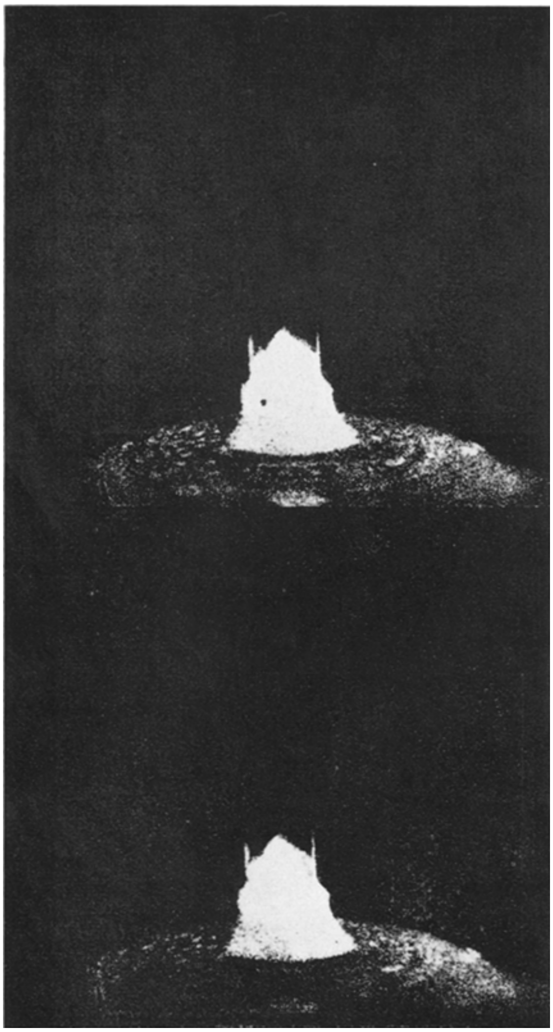

Figure 3 Motion picture sequence showing filament growth at 20 cm/min. Only two dendrites are noted at the solid/liquid interface.

decreases and their size increases ($\sim$ 0.002 to 0.006 cm long). At 20 cm/min (Fig. 3) only two dendrites are observed. These dendrites are $\sim$ 0.006 cm long and $\sim$ 0.009 cm wide at their bases.

Although continuous observation of the growing "circular" filament was made from only one direction, at no time during the study of dendritic growth was propagation by means of a single dendrite tip observed. The individual dendrites maintain their positions for periods which can be measured in seconds. For example, only an occasional dendrite will be observed to move radially or grow out within a 5 sec period. These latter statements are especially pertinent at faster growth rates where the number of dendrites observed is small. At growth rates greater than about 12 cm/min, the growth interface pulsates rapidly (flickering motion) in the direction of growth. Concurrently, large voids are noted between adjoining dendrites.

Detailed examination of Figs. 1 to 3 indicates that the shape of the molten Al_2O_3 pool, from which the filament is withdrawn, is significantly different from that observed at slower growth rates. During dendritic growth the filament grows from a molten meniscus which, although concave near the die surface, may be a parallel sided "cylinder" near the growth interface (see Fig. 9). This latter meniscus geometry is only observed during dendritic growth and is contrary to the relationship between meniscus height and filament diameter introduced in an earlier paper for growth in the range 2.5 to 7.5 cm/min [1]. Including the cylindrical portion of the molten growth pool, meniscus heights of up to 0.02 cm have been recorded. These heights compare with a maximum of 0.0075 cm at slower growth rates. It should be noted, however, that with

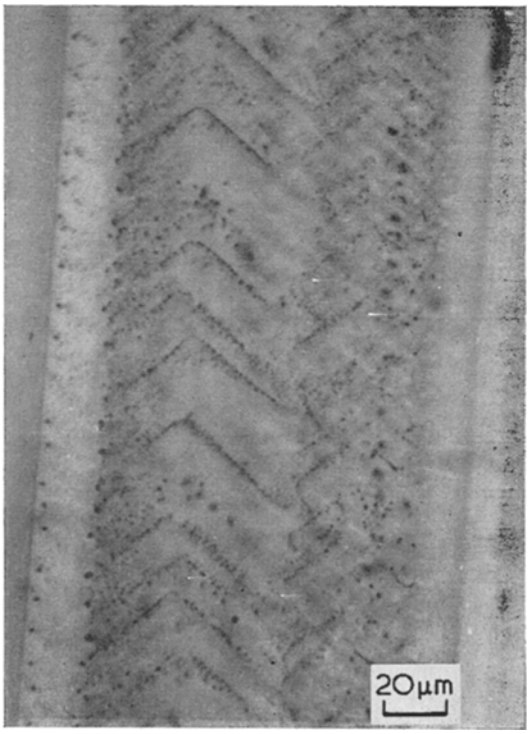

Figure 4 Longitudinal transmission photomicrograph of filament grown at approximately 15 cm/min.

regard to the concave portion of the meniscus, maximum thicknesses comparable with that measured at slower rates, are obtained.

3.2. Micrography

Transmission photomicrographs of filament grown at approximately 15 and 22 cm/min are presented in Figs. 4 and 5, respectively. Circularly shaped voids are observed at 15 cm/min. Elongated irregular shapes are noted at 22 cm/min. In both cases, and in all other dendritically grown samples examined, the voids lie in arrays which, although more complex than those observed in material grown at speeds up to 7.5 cm/min, make similar angles of about 55° with the growth axis. These angular values are in agreement with measurements of the angles between rhombohedral surface planes and the *c*-axis using sapphire crystal dendrites and two circle optical goniometry [5]. However, unlike the conical void arrays observed at slower speeds (Fig. 9b), the apices of the cones in dendritic filament point away from the growth interface.

SEM's taken at a growth interface retained when a filament was pulled free at a growth rate in excess of 25 cm/min, are presented in Figs. 6 to 8. Fig. 6 shows two dendrites and is clearly representative of the type of interface present when growth is occurring as recorded in Fig. 3. Evidence of side arm growth has also been retained at this interface. An end-on view of this retained growth interface is given in Fig. 7 and suggests that solidification between the dendrites takes place by means of the growth of interleaving layers. Although the dendrite tips themselves are

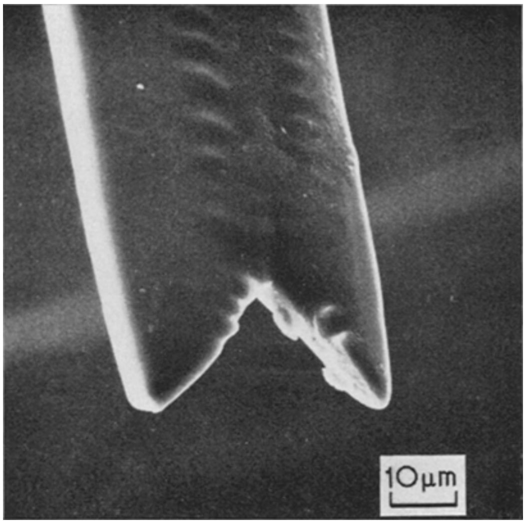

Figure 6 SEM of an interface retained when the filament pulled free at a growth rate in excess of 25 cm/min. Note the presence of only two primary dendrites and the evidence of side growth.

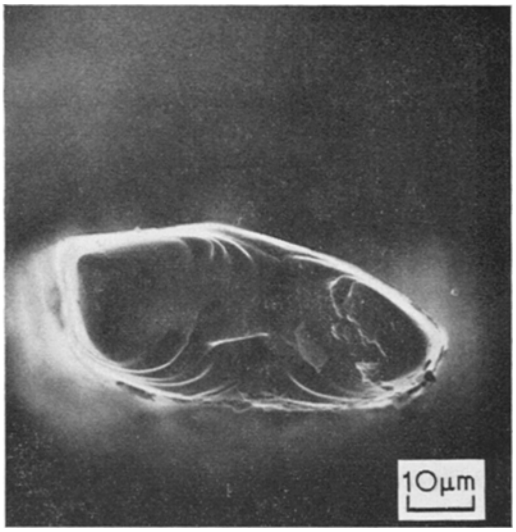

Figure 7 An end-on SEM of the interface presented in Fig. 6.

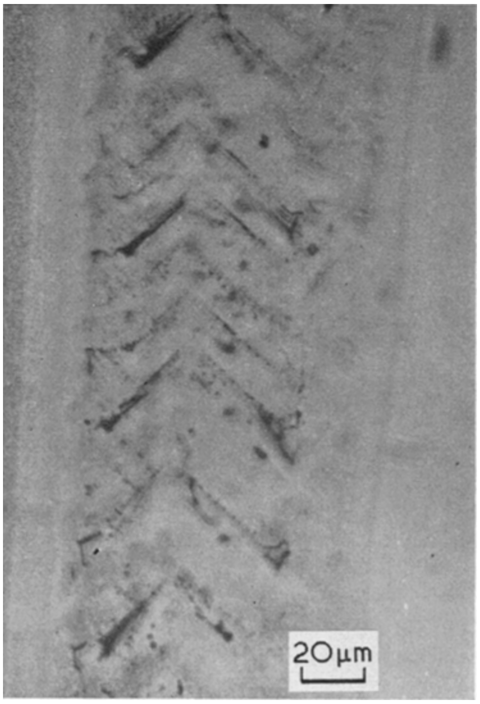

Figure 5 Longitudinal transmission photomicrograph of filament grown at approximately 22 cm/min.

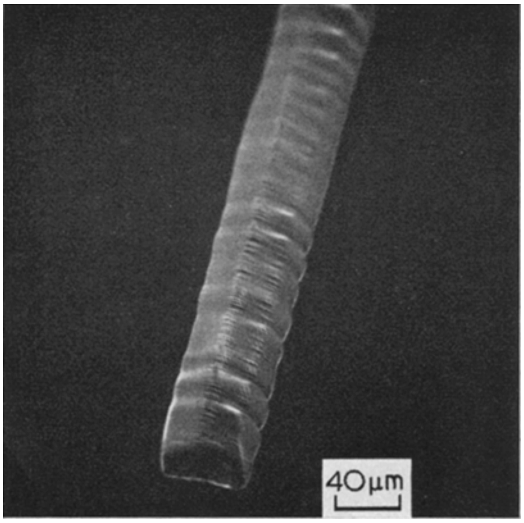

Figure 8 SEM showing the variation in diameter along the length of the sample associated with the pulsating nature of growth.

noted to have triangular cross sections in the SEM examinations, the overall cross section of the filament is polygonal with a strong indication that it is hexagonal. This is in contrast to dendritic growth at slower speeds, involving more than two dendrites, where a distinctly triangular cross section has been noted. An overall SEM of the filament is shown in Fig. 8. Two important features should be noted. This SEM suggests that the cross section of the filament is hexagonal and, secondly, that the diameter of the filament is not constant, but is periodically necked down. The latter feature is not associated with the interface pulsing motion described in Section 3.1. It is more probably the result of a liquid supply problem caused by a jetting action, via the feed-hole of the orifice, at high growth rates.

4. Discussion

Five liquid/solid interface types; planar, facetted, cellular, multiple dendritic and binary dendritic, have been observed, or deduced, to be present during filamentary sapphire growth at increasing speed. These interfaces are drawn schematically in Fig. 9. The void production mechanisms at non-dendritic speeds have been discussed elsewhere [1, 7] and were deduced from direct observation during growth combined with transmission optical microscopy of as-grown samples. The relationship of the void formation mechanism to the growth interface is least obvious in the case of dendritic growth. In this instance, the dendrites maintain essentially fixed

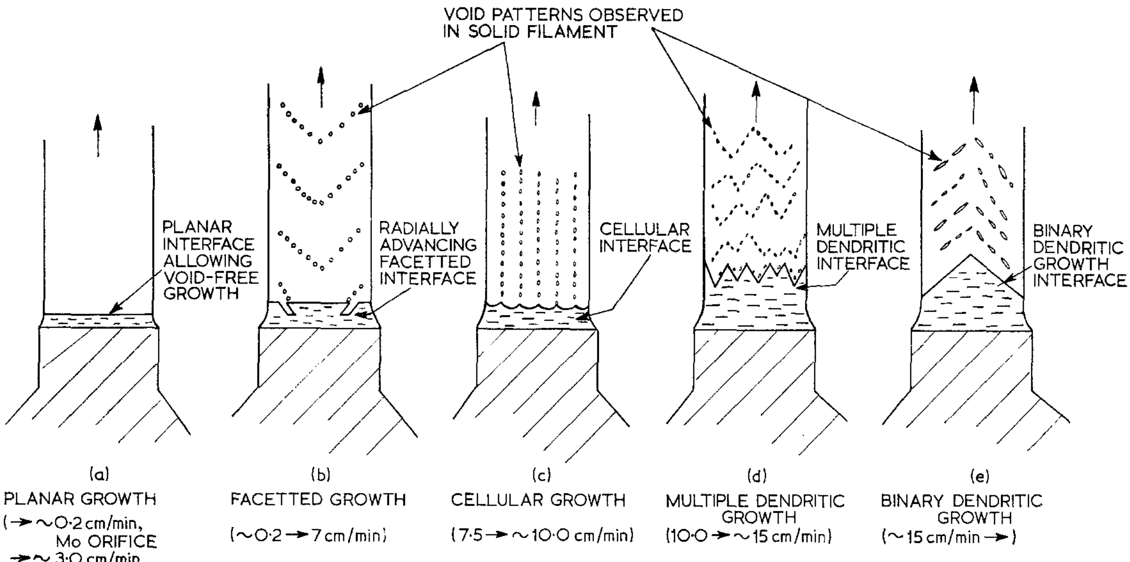

Figure 9 Schematic diagram depicting in an idealized form the void patterns associated with the five solid/liquid interfaces present during growth in the range 0 to 25 cm/min.

positions in the melt (like the cells during growth in the range 7.5 to 10.0 cm/min, Fig. 9c), but produce void patterns related to the rhombohedral planes in *c*-axis sapphire (like those produced by similarly oriented *moving* facets at speeds up to 7.5 cm/min, Fig. 9b). It is suggested that the voids are the result of solidification of liquid trapped behind and between side arms of the primary dendrites. This mechanism for retaining liquid behind the advancing solid interface, taken together with the pulsating nature of growth at fast rates, offers an explanation for the crystallographically related void arrays observed in dendritically grown material.

The considerable extent to which the meniscus growth region is supercooled during dendritic growth has been previously reported [1, 5]. The pulsating character of dendritic growth is related to the degree of supercooling necessary to maintain the fast growth rate. Heat of solidification, liberated as a result of the rapid advance of the interface, causes the liquid temperature immediately in front of the dendrites to rise and their growth to slow down. A significant time is required for heat dissipation throughout the meniscus to occur, and re-creation of the thermally supercooled conditions for a subsequent accelerated growth period.

An estimate of the interface oscillation rate may be generated from the spacing of the void layers observed in micrographs of filament grown at different rates, i.e. assuming each void layer is the result of an interface movement. Using this approach, 10 to 100 oscillations/sec have been calculated for filament grown in the range up to 20 cm/min. The void layer spacings near the interface shown in Fig. 6 indicate that the rate was approximately 400 oscillations/sec.

The breakdown at dendritic growth rates of the relationship between meniscus height and filament diameter reported in an earlier paper [1], may also be related to this oscillatory motion of the growth interface. A secondary role is possibly played by the dendrites themselves which extend into the melt and provide recesses for the vertical support of the meniscus fluid. This explanation is not, however, entirely sufficient, since considerable meniscus heights are observed at slower dendritic growth rates (see Fig. 1), where the dendrites do not extend deep into the melt.

Finally, it was previously suggested [5], as a result of examination of a retained interface containing many dendrites (10 dendrites located on the sides of a distinct triangle), that adjacent pairs of dendrites were related and grew in a complementary manner. This hypothesis has been strengthened by the evidence of the present work pointing to a minimum of two dendrites being required for propagation, and suggests that growth has taken place by means of a twin related mechanism of the type proposed by Hamilton and Seidensticker [8] in germanium.

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References

1. J. T. A. POLLOCK, *J. Mater. Sci.* **7** (1972) 631.
2. H. E. LA BELLE JUN and A. I. MLAVSKY, *Mat. Res. Bull.* **6** (1971) 571.
3. H. E. LA BELLE JUN, *ibid* **6** (1971) 581.
4. B. CHALMERS, H. E. LA BELLE JUN, and A. I. MLAVSKY, *ibid* **6** (1971) 681.
5. H. E. LA BELLE JUN and J. T. A. POLLOCK, *ibid* to be published.
6. J. T. A. POLLOCK, *J. Mater. Sci.* **7** (1972) 649.
7. *Idem, ibid* **7** (1972) 787.
8. D. R. HAMILTON and R. T. SEIDENSTICKER, *J. Appl. Phys.* **31** (1960) 1165.

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