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Filamentary sapphire

Part 3 *The growth of void-free sapphire filament at rates up to 3.0 cm/min*

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The "edge-defined, film-fed growth" (EFG) technique was used to grow filamentary sapphire from tungsten growth orifices in the ⟨0001⟩ growth direction. The higher thermal conductivity of tungsten, compared with molybdenum orifices, results in more efficient heat removal at the growth interface and allows the stable growth of filamentary sapphire at rates up to 15 cm/min. More important, at rates as high as 3.0 cm/min, sapphire was grown entirely free of microvoids. This void-free sapphire acted as a light pipe and had average tensile strength as high as 3.3×10^9 N/m^2 (480×10^3 lb/in.^{2}). The role of tungsten in creating the planar solid/liquid growth interface necessary for void-free growth was investigated using tungsten orifices having different ratios of feed capillary to outside diameter. Finally, the conditions necessary for void-free growth are discussed in terms of the thermal generation and heat transfer processes occurring within the liquid film from which the crystal is withdrawn.

1. Introduction

Details of a novel crystal growth process called "edge-defined, film-fed growth" (EFG) have recently been made available in the literature [1-4]. This technique allows the growth of a variety of cross-sectional shapes by making use of a shaped die. A liquid pool, from which the crystal is withdrawn, is formed on the top planar surface of the die and fed by capillaries which extend down through the die into a liquid reservoir. The crystal shaping or edge definition is maintained by the geometry of the top surface of the die and the fulfilment of a contact angle requirement ($\theta < 90$) between the liquid and the material from which the die (orifice) is fabricated.

The EFG method has been extensively investigated by the growth of 0.025 cm diameter, ⟨0001⟩ growth axis, filamentary sapphire. Details of the growth, microstructure and strength in tension of this sapphire have been presented in the literature [5, 6]. The latter studies, and earlier work [4], were carried out using growth orifices (see fig. 1) fabricated from molybdenum. It was demonstrated that growth stability and the solidification mechanisms were dependent on a thermal balance between the various thermal generation and transfer processes occurring within the growth meniscus film. Except at very slow growth rates (< 0.1 cm/min), the sapphire grown contained microvoids $\sim$ 1 μm diameter arranged in patterns which were dependent upon growth speed. These microvoid patterns were interpreted as characteristic of growth occurring by faceted (up to 7 cm/min), cellular (7 to 10 cm/min), and dendritic (> 11 cm/min) mechanisms at the solid/liquid interface. It was apparent that the role of the orifice in transferring heat into, or extracting heat from, the growth region was an important parameter in creating the temperature gradient at the liquid/solid interface, and thus determining the morphology of this interface.

Tungsten has a substantially higher thermal conductivity, 1.0 W/cm^2/°C, than molybdenum, 0.4 W/cm^2/°C, at 2000°C [7]. This paper describes experiments carried out to investigate the effect of using tungsten growth orifices. In particular, it reports the growth of sapphire, free of microvoids, at rates up to 3.0 cm/min.

2. Experimental

The overall crystal growth apparatus and growth

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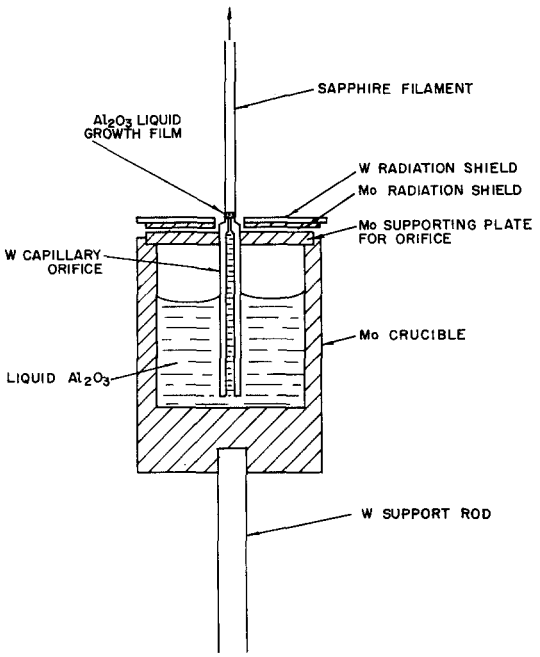

Figure 1 Schematic diagram of crystal growth assembly.

procedures for filamentary sapphire were described in detail in an earlier paper [5]. Fig. 1 is a schematic diagram of the crucible, orifice location plate, growth orifice, and heat shielding arrangement, which comprised the growth assembly used during the present work. Substitution of a tungsten orifice (0.026 cm o.d. × 0.013 cm i.d.) was the only change from the assembly used in the previously described work [5]. Crystal growth was carried out in an argon atmosphere maintained within a water-cooled quartz furnace [8]. Heating was by rf induction coupling to a graphite susceptor, within which the Mo crucible was located. When the crucible and Al_2O_3 charge (crushed Vernueil boules) were heated to above the melting temperature of Al_2O_3, the molten Al_2O_3 rose to fill the feed hole by capillary action. A ⟨0001⟩ growth axis, filamentary sapphire seed was then lowered into contact with the molten Al_2O_3 in the feed hole. After adjustment of melt temperature and seed withdrawal rate, the molten Al_2O_3 spread across the top surface of the orifice, and growth of a sapphire filament from the thin meniscus film shown in fig. 1 was established.

The ⟨0001⟩ growth axis, and single crystal nature of the sapphire grown, was confirmed by Laue X-ray diffraction. After immersing samples in oil of refractive index close to that of sapphire (n_e = 1.760, n_o = 1.768), metallographic examination of the filament was carried out using transmitted light.

3. Results

Filamentary sapphire was grown at rates between 1.5 and 25.0 cm/min. Although it is the primary purpose of this paper to discuss growth at speeds up to 3 cm/min, it will be useful to present briefly some details of growth at fast rates.

Growth at fast rates from a tungsten orifice was more stable, with respect to uniformity of the filament cross-section, than growth from a similar molybdenum orifice. For example, when growth was carried out continuously at 15 cm/min, the filament cross-section, although no longer circular, maintained an almost constant rounded triangular shape. At these growth rates, solidification takes place by a dendritic mechanism, details of which were recorded using 16 mm motion photography [9]. Therefore, compared with a molybdenum orifice, the higher thermal conductivity of the tungsten orifice allowed a more effective, and uniform, thermally supercooled liquid environment to be created in front of the advancing dendrites.

As the growth rate was reduced (< 10 cm/min), growth by a cellular mechanism was noted. On further reducing the growth rate to

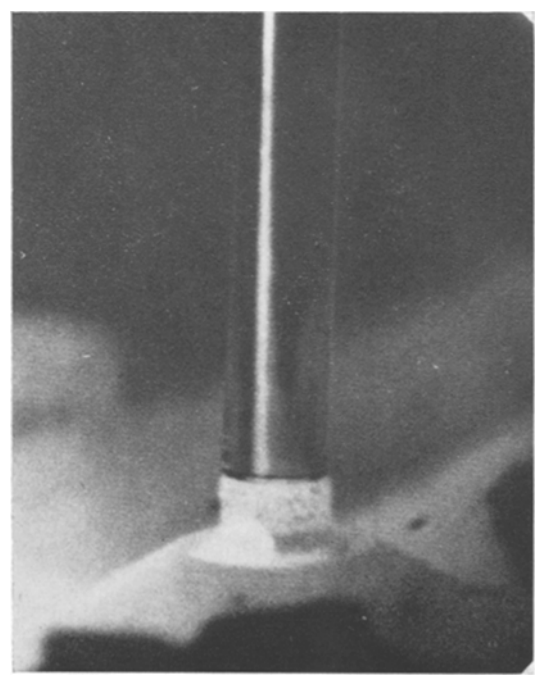

Figure 2 Photograph recording void-free filament growth at 3.0 cm/min from a tungsten growth orifice.

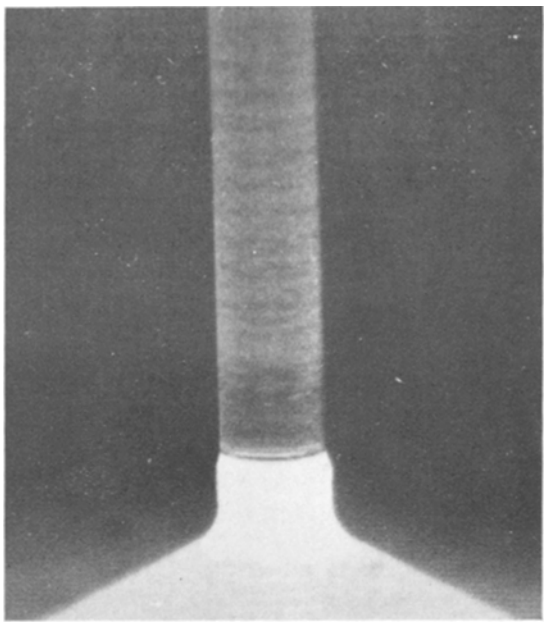

Figure 3 Photograph recording the growth of voided filament at ~ 3.0 cm/min from a molybdenum growth orifice.

6 cm/min, growth by means of a mechanism involving a radially advancing facet was observed. The latter two growth mechanisms have been observed during growth from molybdenum orifices and result in distinctive microvoid patterns, details of which have been published [5]. Growth by means of a facet mechanism still occurred with the tungsten orifice at rates down to 3.4 cm/min. However, on reducing the growth rate to 3.0 cm/min, it was noted, after a few minutes of growth, that the position of growth rate change was marked with scattered light. The sapphire filament growing at 3.0 cm/min was of sufficient optical quality to act as a light pipe, and light transmitted through it from the meniscus film region was scattered at the junction where filament grown at 3.4 cm/min, and containing 1 μm diameter voids, started. Figs. 2 and 3 are photographs of filament growing at ~ 3 cm/min from tungsten and molybdenum orifices, respectively. The difference in the optical quality of the sapphire is evident.

Small lengths of void-free material have been grown occasionally at speeds around 2.5 cm/min from molybdenum orifices, usually when the orifice tip is below the top of the radiation shielding (see fig. 1). However, it has never been possible to reproduce these growth conditions, and only a few inches were grown. With tungsten orifices, it was possible to grow several feet of void-free sapphire and to introduce changes in growth rate, resulting in the growth of alternate lengths of light pipe quality or voided filament. During continuous growth at 3.0 cm/min, small clusters of voids appeared at intervals roughly 3 to 5 ft apart. These voids were marked by scattered light.

The growth of void-free filament was repeated using several tungsten orifice assemblies. In each case, growth rates of 3.0 cm/min, or less, together with a low melt temperature, resulted in the growth of void-free material. This void-free material suffered from the disadvantage that it was not entirely linear, and exhibited slight curvature over 12 in. lengths. This curvature was the result of the very thin meniscus film from which it was grown.

A transmitted light photomicrograph of the void-free sapphire is shown in fig. 4. For comparison, a typical photomicrograph of filament grown from a molybdenum orifice, and containing microvoids lying in or near the sapphire $\{10\bar{1}2\}$ planes, is shown in fig. 5. A transmitted

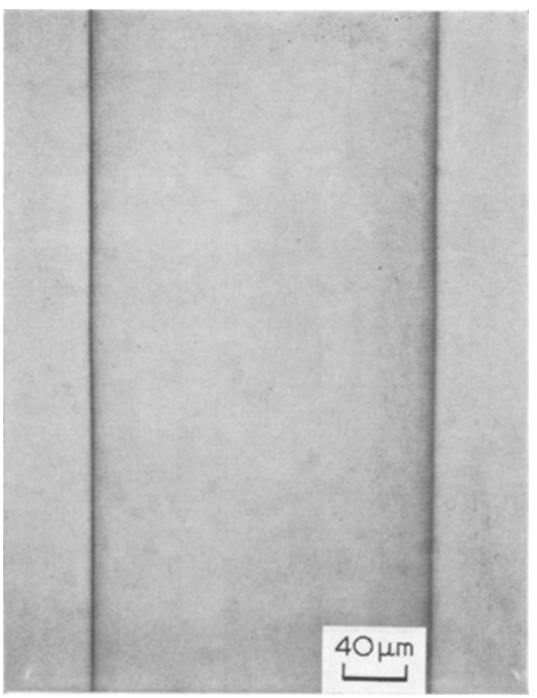

Figure 4 Longitudinal transmission photomicrograph of void free sapphire filament.

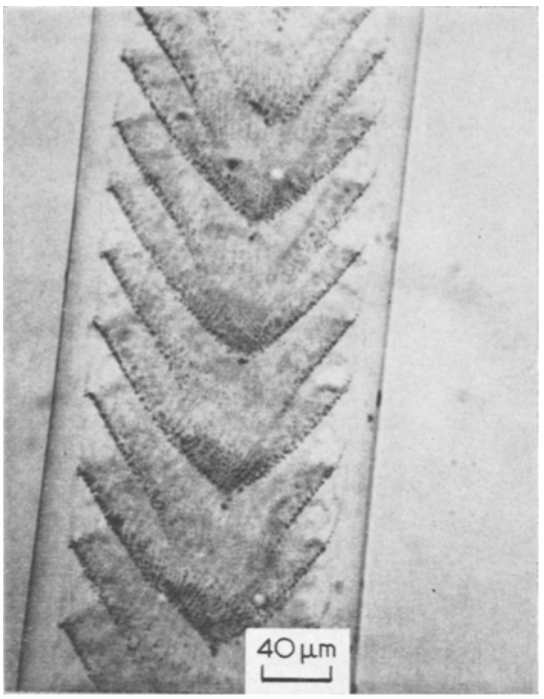

Figure 5 Longitudinal transmission photomicrograph of void free sapphire filament containing microvoids lying in or near {10$\bar{1}$2} planes (growth speed ~ 3.0 cm/min).

light photomicrograph of filament grown at 3 cm/min with a tungsten orifice, from a thicker meniscus growth film, i.e. higher melt temperature, is shown in fig. 6. Linear arrays of voids near the periphery of the filament were noted.

In order to investigate further the role of the tungsten orifice in creating the growth conditions for void-free filament, growth was carried out using 0.026 cm o.d. orifices having feed capillaries of 0.007 and 0.020 cm diameter, respectively. In this way, the surface area of tungsten available for heat transfer within the growth meniscus film was varied. Growth of void-free material could not be obtained using the 0.020 cm diameter feed capillary at rates down to 1.25 cm/min. Using the 0.007 cm diameter feed capillary orifice, clear filament could be easily grown, although not at a faster rate than at that previously available. However, growth from a slightly thicker meniscus growth film was possible using the 0.007 cm diameter feed capillary orifice, and the void-free filament grown was free from the excessive bending present in filament grown from the tungsten orifices having 0.013 cm diameter feed capillaries.

The fracture strength of the void-free material was measured in tension using samples having 2.5 cm gauge lengths and a strain rate of 0.005 min^{-1}. Average tensile strengths of up to 3.3 × 10^9 N/m^2 (480 × 10^3 $lb/in.^2$) were measured in filament which had been carefully handled to avoid surface abrasion. This is the highest average tensile strength value measured in as-grown sapphire, other than very small diameter whiskers [10], and compares with 2.75 × 10^9 N/m^2 (400 × 10^3 $lb/in.^2$), for filamentary EFG sapphire containing microvoids [6].

4. Discussion and conclusions

Void-free sapphire filament may be grown using a tungsten growth orifice when three criteria are satisfied: (1) the ratio of orifice outside diameter to the diameter of the feed capillary is 2.0 or greater, (2) growth is carried out at 3.0 cm/min, or less, and (3) the liquid film from which the filament is withdrawn is 0.001 cm or less.

It was shown in an earlier paper [5] that, because of the very fast growth rates achieved

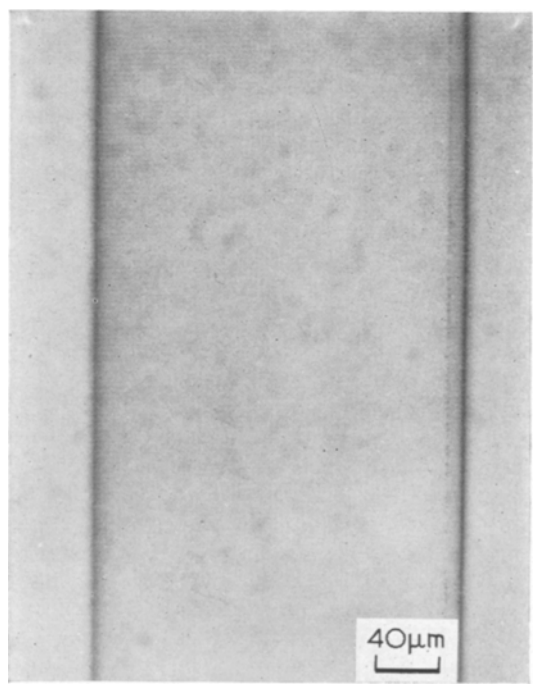

Figure 6 Longitudinal transmission photomicrograph of almost void-free sapphire filament grown with a tungsten orifice at a slightly higher melt temperature than that used for void-free growth. Linear arrays of voids are noted near the periphery of the sample.

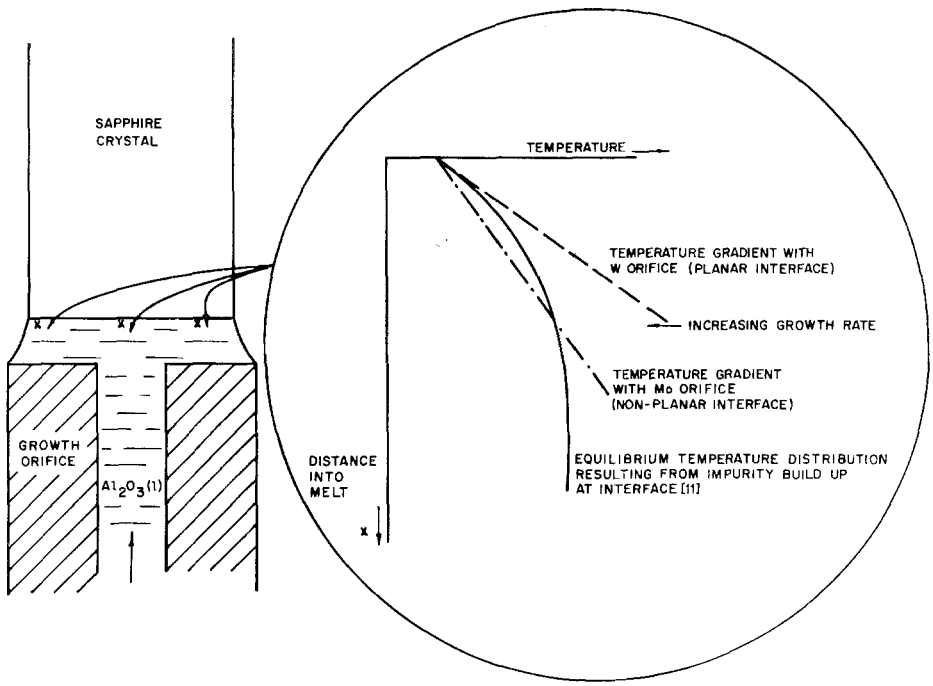

Figure 7 Schematic diagram comparing temperature distributions at the solid/liquid interface obtained with Mo and W orifices to the equilibrium distribution arising from the rejection of impurities into the liquid.

with EFG, the possibility of constitutional supercooling may not be ruled out, even though the impurity concentration in the sapphire grown is less than 100 ppm. Also, it has been demonstrated that at fast growth rates, growth occurs by dendritic propagation into a liquid melt, the thermally supercooled nature of which has been measured [1, 5]. When either thermal or constitutional supercooling of sufficient magnitude occurs, breakdown of the solid/liquid interface is obtained, and microvoids result.

Growth of void-free material implies that the conditions for growth by means of a completely planar solid/liquid interface were created. Since this condition could not be achieved at similar growth rates with molybdenum orifices, it may be concluded that the higher thermal conductivity of tungsten allows a positive temperature gradient from the liquid meniscus to the solid crystal to be created. This gradient is of a magnitude sufficient to suppress any incipient breakdown of the planar interface due to impurity controlled constitutional supercooling (see fig. 7). The temperature gradient at the interface is strongly dependent on conduction from the top surface of the orifice across the thin growth film. It is for this reason that the ratio of orifice diameter to feed capillary diameter has to be greater than ~ 2.

The maximum growth rate for void-free filament of 3.0 cm/min, obtained during the present work is a significant indication of the delicate balance between the thermal transfer and generation processes occurring within the growth region. Ignoring heat losses by radiation from the meniscus surface, Chalmers *et al* [3] showed that growth by means of a planar interface was dependent on the sapphire crystal being the sole means of extracting heat from the growth region. They calculated that the maximum growth rate at which the void-free crystal, acting as a light pipe, could remove all the heat of solidification was 2.4 cm/min. This assumed zero heat transfer across the growth film from the die. The calculated value is very close to the experimentally measured maximum growth rate of 3.0 cm/min reported here. At faster growth rates, the liquid in front of the advancing interface has to be supercooled or the temperature gradient reduced (see fig. 7), by lowering the melt temperature, in order to avoid reduction of the filament diameter. This causes the conditions for faceted or cellular growth to be created, together with the production of microvoids.

The role of the very thin meniscus growth film becomes clear on consideration of the heat loss mechanisms available during EFG. Heat loss by radiation from the surface of the meniscus is an increasingly important parameter as the film thickness increases [5]. This causes thermal supercooling in the liquid melt above the outer edge of the orifice. In the extreme case, growth by means of a radially moving facet is observed. The peripheral arrays of microvoids, observed in filament grown from a meniscus film only slightly thicker than that from which void-free filament was grown (fig. 6), confirm the role of radiation heat loss. Evidently, under these growth conditions, only the outer edge of the growth region is sufficiently cooled to allow facet formation, a more positive temperature gradient being maintained at the centre of the growth interface.

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