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Crystal growth of sapphire filaments by a laser-heated floating zone technique

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A laser-heated floating zone technique is employed to grow a filamentary *c*-axis sapphire. Crystal growth is directly recorded during the process by photography, and crystals grown under various conditions are examined by means of a transmission optical microscope to obtain the relationships between microvoid formation and growth conditions. Observations of filaments indicated that the microvoid results from shrinkage due to dendritic growth. Microvoids are eliminated by choosing a growth rate less than 4.7 cm h^{-1} or by focusing the laser beam. By using this method, a void-free filament of 1.4 mm diameter is obtained.

1. Introduction

The microvoid is the most striking characteristic of a sapphire filament, and it adversely affects its properties because of light scattering. The mechanism for microvoid formation has been investigated in detail in the crystal growth of sapphire filaments by the EFG (edge-defined, film-fed growth) method [1–4]. In this experiment, the pulling rate had the most significant effect on the void formation, and a void-free sapphire filament was grown at a slow pulling rate. However, the use of a molybdenum crucible and dies in the EFG method limited such growth conditions as ambient atmosphere.

Another possible method is the laser-heated floating zone process [5]. In this method, a laser is adopted as a heat source, so it is possible to grow a sapphire filament under various growth conditions. For example, sapphire can be grown in air or at a reduced pressure. For this reason it was expected that a void-free sapphire filament could be grown easily. Moreover, this method is advantageous in that the void formation in the crystal can be observed directly during the growth process. The purpose of this paper is to observe void formation during the growth of the sapphire filaments by the laser-heated process and to examine the relationship between the formation of voids and the growth conditions.

2. Experimental details

The crystal growth apparatus used in this experiment was that originally designed and developed by Haggerty [6]. A continuous-wave CO_2 laser with a maximum output of 375 W was employed. After a laser beam was split into two beams by a mirror, these beams were focused on both sides of a feed rod by means of gallium arsenide lenses. The diameter of the incident laser beam on the surface of the feed rod was 1.5 mm. The feed rod, 2 mm square, was cut from a sapphire single crystal grown by the Czochralski method. The *c*-axis [<0001>] was chosen as the filament axis. The feed rod was set on the upper holder and a seed crystal was set on the lower holder. The seeding process was carried out as follows: a molten drop was formed at the end of the feed rod by the focused laser beams, and the seed crystal was then contacted to the drop. During crystal growth, the feed rod and seed crystal were driven down at different rates: the feeding rate of the upper rod was one half that of the pulling rate of the seed crystal. Thus, in the series of experiments the diameter of the grown filament could be fixed at 1.4 mm. Crystal growth was carried out in air and also at reduced pressure (10 mm Hg). It was very advantageous to use the laser-heated process in order to observe the molten zone during growth, because no obstacle such as the r.f. coil used in the EFG

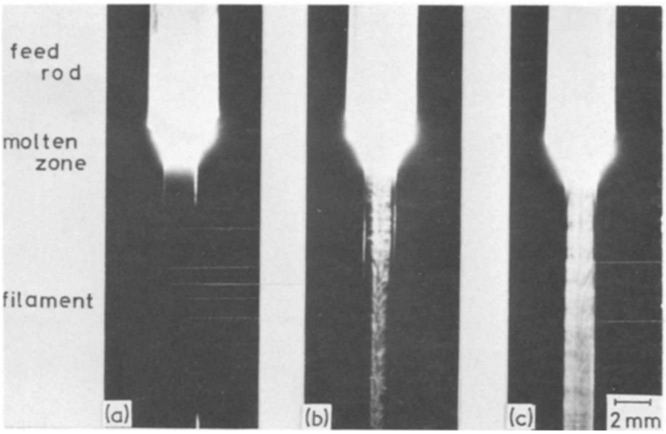

Figure 1 Photographs recording the growth of sapphire filaments at various growth rates: (a) 9.5 cm h^{-1} (b) 19.4 cm h^{-1}, (c) 29 cm h^{-1}.

method, is present in the furnace. Furthermore, since sapphire is transparent, the behaviour of the void formation during the filament growth could be clearly observed and recorded on a single frame photograph. In addition to direct observation, samples of filamentary sapphire grown under various conditions were examined using a transmission optical microscope.

3. Results

3.1. Relationship between pulling rate and void formation

The relationship between the pulling rate and void formation was examined by varying the pulling rate in the range 4.7 to 47 cm h^{-1}. However, the ratio of feeding rate to pulling rate of the grown filament was kept constant in order to obtain a filament with the same diameter throughout the experiments. Neither the feed rod nor the filament was rotated.

Representative patterns of voids formed in the filaments during the growth at various pulling rates are shown in the Fig. 1. At a low pulling rate, the filament was transparent with few voids, as shown in Fig. 1a. However, as the pulling rate was increased, many voids suddenly appeared and the filament became opaque as result of light scattering from the voids. The number of voids increased in proportion to the pulling rate.

The distribution of voids in the grown filaments observed by transmission microscopy, is shown in Fig. 2. At a pulling rate of 4.7 cm h^{-1}, the filament was free of microvoids as shown in Fig. 2a. However, at 9.5 cm h^{-1}, voids began to appear in the centre of the filament. The size of each void was about 5 μm. At a higher pulling rate, the number

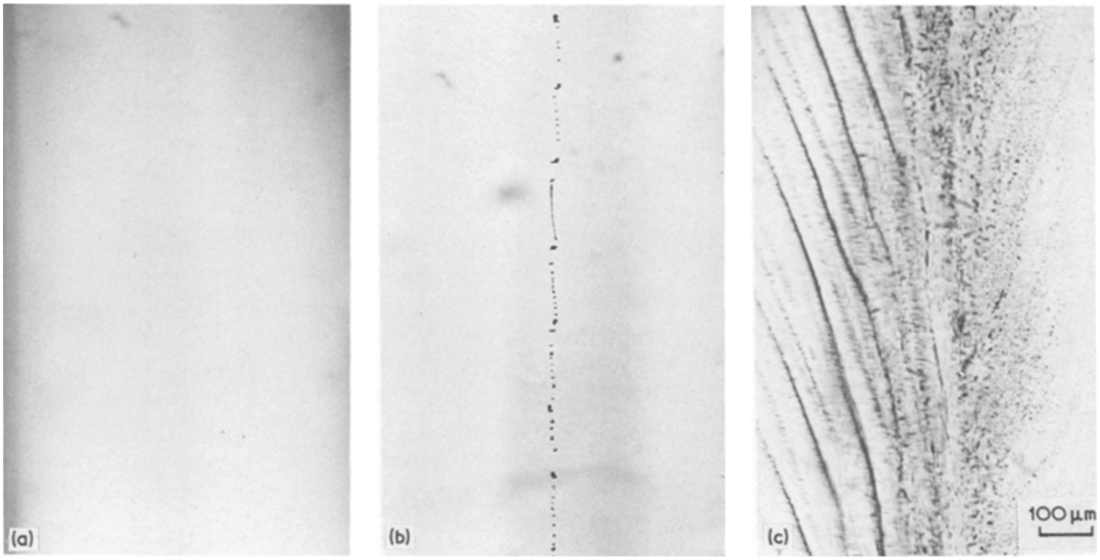

Figure 2 Longitudinal transmission photographs of sapphire filaments grown at various growth rates: (a) 4.75 cm h^{-1}, (b) 9.5 cm h^{-1}, (c) 47 cm h.

of voids increased as shown in Fig. 2c, and they formed a cone whose apex pointed in the growth direction.

3.2. Influence of gas pressure on the formation of voids

In order to determine whether the void formation was due to gas evolution or not, filaments were grown at 10 mm Hg. In this experiment, the pulling rate was 29 cm h^{-1}. The arrays of voids in the filament grown at this pulling rate are shown in Fig. 3. Comparison of the array of voids in the filament grown at a reduced pressure with that grown at 1 atm revealed no difference, and it was assumed that a reduction of pressure played no part in reducing the number of voids present. This suggests that the void formation is not based on gas evolution.

3.3. Effects of the rotation of the feed rod and filament on the void formation

The rotation of the feed rod or filament influenced the condition of the surface of the filament and the void distribution. When neither the filament nor the feed rod was rotated, the grown filament had a smooth surface and had the morphology of a hexagonal cylinder, the plane of which was perpendicular to the *a*-axis.

When the voids formed the cone as mentioned in Section 3.1, the arrangement of the voids was always distorted in such a way that the cross-section of the cone was an ellipse its long axis perpendicular to the laser beam. This characteristic pattern of voids in the filament results from the optical arrangement of the laser apparatus. As the two laser beams were focused on both sides of the molten zone, the temperature of the incident points rose markedly, which gives rise to a two-fold symmetrical temperature distribution. With regard to the temperature distribution, it was expected that the microvoid could be eliminated by rotating the feed rod or the filament. Experiments were carried out by rotating the filament or feed rod at a speed of 18 to 74 rpm and void formation was observed during the crystal growth. When the feed rod and/or the filament was rotated, the surface of the grown filament became wavy, depending on the rotation rate of the molten zone against the laser beams. The pitch of these waves was in inversly proportional to the rotation rate. There was no change in the distribution of voids when the rod was rotated up to 37 rpm, when the filament was rotated, voids were arranged concentrically. The distribution of microvoids was altered by rotation of the feed rod or the filament; however, the number of voids did not vary.

3.4. Effect of laser power on void formation

The intensity of the laser beam affected the tem-

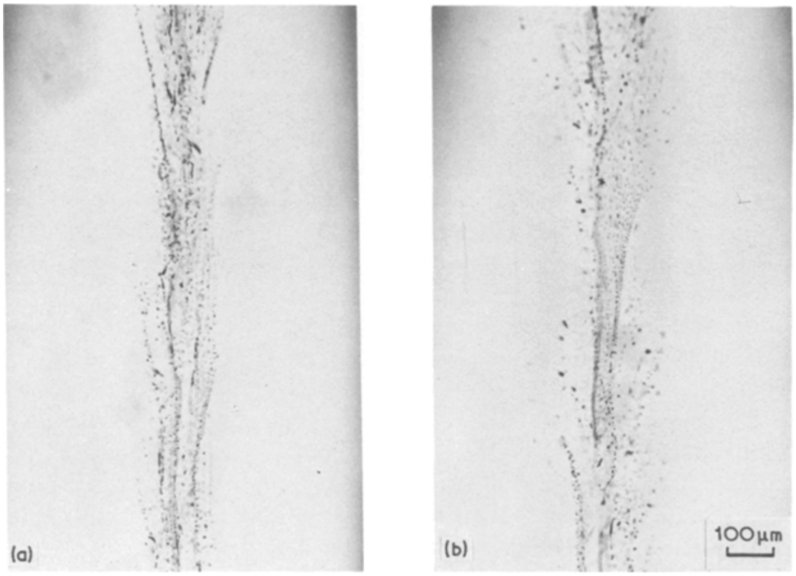

Figure 3 Longitudinal transmission photographs showing the effect of atmosphere on microvoid distribution: (a) at 1 atm (b) at 10 mm Hg.

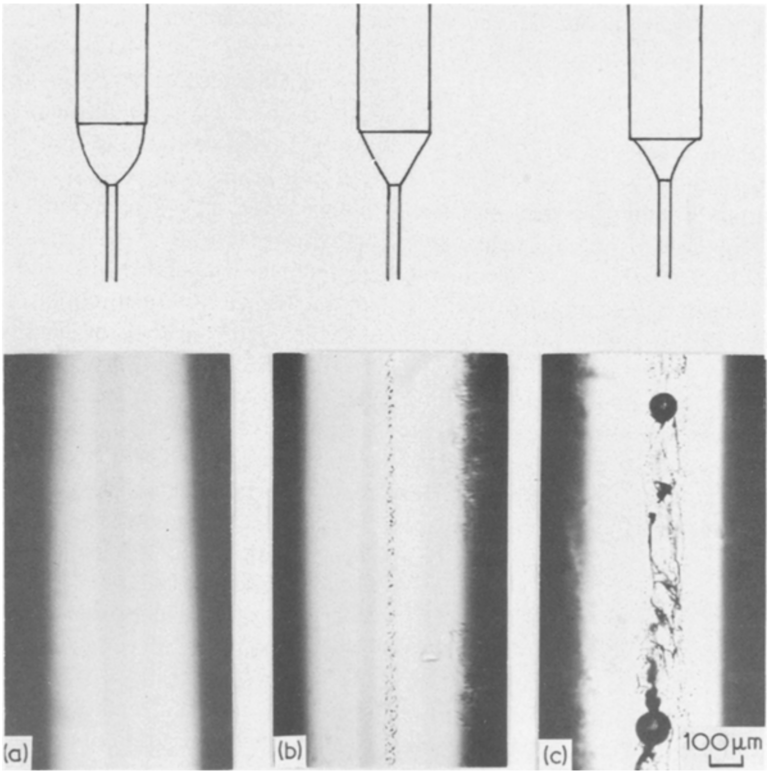

Figure 4 Influence of laser output on the shape of the molten zone and the distribution of microvoids. (a) 100 W, (b) 75 W, (c) 50 W.

perature of the molten zone and its shape. When the laser beam power was high, the temperature of the molten zone rose. The zone became convex and the height of the molten zone increased as shown in Fig. 4a. In this case, no void was present in the filament. However, with increasing height of the molten zone, the filament diameter became unstable.

On the other hand, when the intensity of the laser beam was lowered, the temperature fell and the molten zone became concave (Fig. 4b) causing the generation of voids. When the melt was heated locally by focusing the laser beams, microvoids were not generated in spite of the concave molten zone. This indicates that the formation of microvoids is related to the temperature gradient in the molten zone.

4. Discussion and conclusions

Gas evolution or the trapping of liquid is considered to be the cause of microvoid formation in a sapphire filament. Growth experiments at a reduced pressure indicated that microvoids result from shrinkage due to the large difference in density between liquid and solid sapphire. This result agrees with the observation of microvoids in the filaments grown by the EFG method [2] and also in the boule grown by the Czochralski method [7]. Growth based on the trapping of liquid is characterized by dendritic growth. It is reported that in sapphires with a [0 0 0 1] growth axis, dendrites are bounded by (1 0 1 2) rhombohedra and (0 0 0 1) planes, consequently the microvoids tend to array on rhombohedral planes and form a conical pattern [1].

The pattern of the voids in the filament grown by the laser-heated method is also conical. However, the angle made by the void dispersion with the filament axis (*c*-axis) is random and is not in agreement with the angle of 56° made by $(1 0 \bar{1} 2)$ rhombohedral plane and the *c*-axis. This suggests that a dendritic front may be an origin of these microvoids but that dendrites were formed at random and solidification did not advance in a radially continuous way. This may be due to the two-fold symmetrical temperature distribution in the molten zone.

The development of dendrites is closely related to the thermal supercooling of liquid. Because in the case of the laser-heated technique, the heat source is outside the molten zone and the melt is heated locally, the temperature at the centre of the molten zone is lower than outside and the temperature gradient is small. The degree of thermal supercooling at the centre is, therefore, large, and the void is initially formed at the centre of the filament. The thickness of the thermally supercooled layer depends on the thermal gradient at the solid–liquid interface: the layer becomes thiner with increasing thermal gradient, so it is possible to eliminate the microvoids by focusing the laser beams or by increasing the laser power as mentioned in Section 3.4. In addition to the laser power, the pulling rate has the greatest affect on the development of dendrites. A high pulling rate gives a large degree of supercooling and promotes dendritic growth. Consequently, it is necessary to decrease the pulling rate to produce a void-free filament.

In conclusion, investigations on microvoids in sapphire filaments grown by the laser-heated floating zone technique suggest that microvoids result from dendritic growth. Void-free sapphire filaments 1.4 mm diameter were grown by decreasing the growth rate and focusing the laser beams.

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