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DEVELOPMENT OF SINGLE CRYSTAL BETA  
ALUMINA MEMBRANE

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## ABSTRACT

The feasibility of using a novel crystal growth technique developed by Tyco Laboratories, Inc., for the growth of  $\beta$ -alumina sheaths is investigated. Melt containment components fabricated from Mo, W, and Ir are used and it is concluded that only Ir offers sufficient thermodynamic compatibility with the melt. Rods and tubes are grown and characterized using metallographic and X-ray diffraction techniques. They are found to be two phase, composed of  $\beta$ -alumina with an admixture of  $\alpha$ -alumina. The appearance of the latter phase is due to sodium loss from the melt and it is suggested that 100%  $\beta$ -alumina tubes may be grown using apparatus allowing growth in inert gas pressures of up to 30 atm.



## Table of Contents

|   | Page No. |
|---|----------|
| ABSTRACT .....  | iii      |
| I. SUMMARY .....  | 1        |
| II. INTRODUCTION .....                                    | 3        |
| III. APPARATUS AND BASIC EXPERIMENTAL<br>PROCEDURES ..... | 5        |
| IV. CRYSTAL GROWTH.....                                   | 11       |
| A. Molybdenum Setups .....                                | 11       |
| B. Tungsten Setups .....                                  | 14       |
| C. Iridium Growth Setup .....                             | 14       |
| V. CONCLUSIONS .....                                      | 19       |
| VI. REFERENCES .....                                      | 21       |

Appendix: REPRINTS OF PUBLICATIONS DESCRIBING  
EDGE-DEFINED, FILM-FED GROWTH



## List of Illustrations

| Figure No. |   | Page No. |
|------------|---|----------|
| 1.         | Quartz Furnace Assembly Incorporating Two .....<br>Window Ports   | 6        |
| 2a.        | Schematic Diagram Showing Crucible and Die .....<br>Set-Up Used for Growth of Rods  | 7        |
| 2b.        | Schematic Diagram Showing Crucible and Die .....<br>Set-Up Used for Growth of Tubes   | 7        |
| 3.         | Crystal Growth Apparatus .....  | 8        |
| 4.         | $\beta$ -Alumina Tubes Grown at 8 to 11 In./Hr Using .....<br>Molybdenum Setups   | 13       |
| 5.         | $\beta$ -Al <sub>2</sub> O <sub>3</sub> Rod Grown From Iridium Setup .....  | 16       |
| 6.         | $\beta$ -Al <sub>2</sub> O <sub>3</sub> Rod Grown From Iridium Setup .....  | 16       |
| 7.         | Laue Back Reflection Photograph of Area Shown in .....<br>Figs. 5 and 6   | 17       |
| 8.         | Laue Back Reflection Photograph of Flat Surface of .....<br>Monofrax H $\beta$ -Al <sub>2</sub> O <sub>3</sub> Sliver Platelet Shows {0001}<br>Plane of Hexagonal $\beta$ -Al <sub>2</sub> O <sub>3</sub> | 17       |

## I. SUMMARY

The crystalline and electronic structure of  $\beta$ -alumina is such that, although exhibiting negligible electronic conductivity below 300 °C, it exhibits considerable anisotropy with respect to sodium ion conductivity. It has been proposed that it may have important future application as a membrane for high energy batteries. Ford Motor Company has demonstrated this potential with polycrystalline  $\beta$ -alumina membranes. As well as improvements in efficiency which would accrue from the use of single crystal membranes, lower operating temperatures and freedom from circuit failure due to intergranular processes are additional possible advantages. Thus, the establishment of a method for the growth of single crystalline  $\beta$ -alumina is of considerable interest.

The objective of the present program was to establish the feasibility of growing single crystal  $\beta$ -alumina using the "edge-defined, film-fed growth" technique developed by Tyco Laboratories which allows the growth from the melt of crystals of predefined shape, such as tubes.

Crystal growth was carried out in an argon atmosphere using RF heating, and melt and die components fabricated from Mo, W and Ir. Using single crystal seeds, 0.125 in. diameter rods and 0.20 in. o.d.  $\times$  0.16 in. i.d. tubes were grown from the melt at rates of up to 15 in./hr. As determined by Debye-Scherrer X-ray diffraction, the material grown was  $\beta$ -alumina containing an admixture of  $\alpha$ -alumina. Only iridium components may be used without excessive erosion and dissolution of the crucible and die material in the melt, and subsequent incorporation in the crystals grown. Rods grown using Ir components were free from contamination, and, although two phase, exhibited single crystallinity as determined by X-ray Laue diffraction, indicating that the  $\alpha$ - and  $\beta$ -phases were mutually oriented with respect to each other.

The major problem to be solved is loss of sodium from the melt by volatilization during growth. This is the reason for the appearance of  $\alpha$ -alumina in the samples grown. It is suggested that a furnace be constructed such that  $\beta$ -alumina tubes may be grown in inert atmosphere pressures of up to 30 atm, thus suppressing the loss of volatile components during growth.





## II. INTRODUCTION

$\beta$ -alumina has for some time been in widespread use as a refractory material in the form of cast bricks. More recently, it has been proposed that it may have important future application as a membrane for high energy batteries. Ford Motor Company has demonstrated this potential with polycrystalline  $\beta$ -alumina membranes and a liquid sodium-liquid sulphur system.<sup>1</sup>

The property of  $\beta$ -alumina which allows it to be considered for this function is the anisotropy which its crystalline structure exhibits with respect to ionic conductivity, electronic conductivity being essentially negligible in all directions.<sup>2</sup> At room temperature, it is virtually nonconducting along the c-axis of the hexagonal cell, yet has a specific resistance of only 30 ohm-cm at right angles to this direction, i.e., along the a-axis. Obvious advantages in efficiency compared with polycrystalline aggregates will accrue from the use of single crystalline membranes of the correct orientation. Even if the polycrystalline aggregates are of preferred orientation, the presence of grain boundaries provides additional problems, since intergranular processes may occur, resulting in failure of the conducting path. Also, it is possible that lower operating temperatures may result from the use of single crystal materials. Thus, the establishment of a method for the growth of single crystalline  $\beta$ -alumina is of considerable interest.

The objective of the present program was to establish the feasibility of growing single crystal  $\beta$ -alumina by making use of a novel crystal growing technique developed by Tyco Laboratories, Inc.<sup>3,4\*</sup> This technique has been developed primarily with the growth of sapphire ( $\alpha$ -alumina) and allows the growth of crystals with constant, but almost arbitrary, cross-sectional shape. In addition to producing single crystals, the method, if successfully applied to  $\beta$ -alumina, would allow the production of  $\beta$ -alumina sheaths in forms most suited for battery use. These sheaths would allow the fabrication of plates containing a minimum quantity of, for example, liquid sodium. By this method, the bulk of the sodium could be held in a container away from the liquid cathode or catholyte, and transported to the  $\beta$ -alumina sheath for reaction by capillary action.

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\*See Appendix.

This report describes experiments and results whose goal was the establishment of a melt growth approach to the production of single crystalline  $\beta$ -alumina sheaths.

### III. APPARATUS AND BASIC EXPERIMENTAL PROCEDURES

The double window-port quartz furnace assembly<sup>5</sup> shown schematically in Fig. 1 was used for all crystal growth experiments. Schematic diagrams of the setups used for the growth of rods and tubes are presented in Fig. 2. The overall system including furnace, stereomicroscope viewer, pulling system, etc., is shown photographed in Fig. 3. An inert atmosphere, argon in the present case, is maintained within the furnace, which consists of two concentric quartz tubes between which cooling water flows. The melt and growth area is viewed directly through either of the ports which allow essentially undistorted observation. The window-ports are provided with a cover of optical quality glass. The inert gas flow (2) acts to prevent oxide deposition on the inside of the window and thus maintains clean observation conditions. The two ports are separated by 120° of arc. They allow both temperature measurements and control, and optical monitoring of the growth procedures. They are at angles of 90° and 60° to the furnace axis in order to provide additional observation freedom of the area of interest.

A 450 Kc induction unit is used to raise the crucible containing the melt to the necessary growth temperature either by susception directly to the crucible or a susceptor surrounding it. Crucibles and dies were fabricated from molybdenum, tungsten, and iridium and will be described in the following appropriate sections. The pulling mechanism may be simply considered as two rigid parallel vertical shafts on one of which is an air bearing connected to a plate with guide bearings on either side of the opposite shaft. Using compressed air, the system is essentially frictionless. A ball disk integrator and synchronous motor are used to move the shaft holding the seed crystal. The length of growth available is ~30 in. and constant growth speeds in the range 0.001 to 38 in./hr may be selected. In order to maintain a beneficial furnace atmosphere and to prevent backstreaming of air into the system via the pulling rod exit, an expandable bellows arrangement was used as shown in Fig. 3.

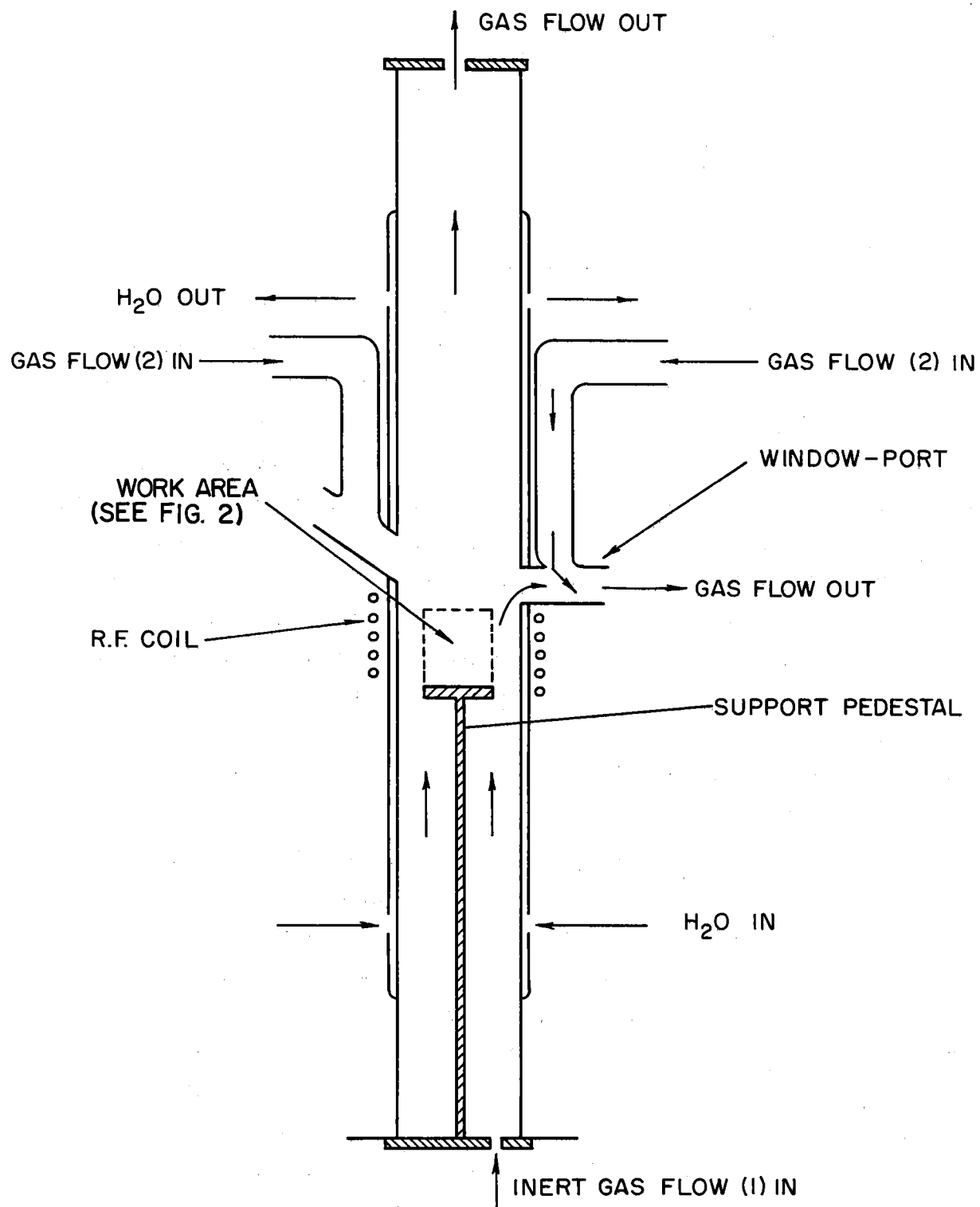


Fig. 1. Quartz furnace assembly incorporating two window ports

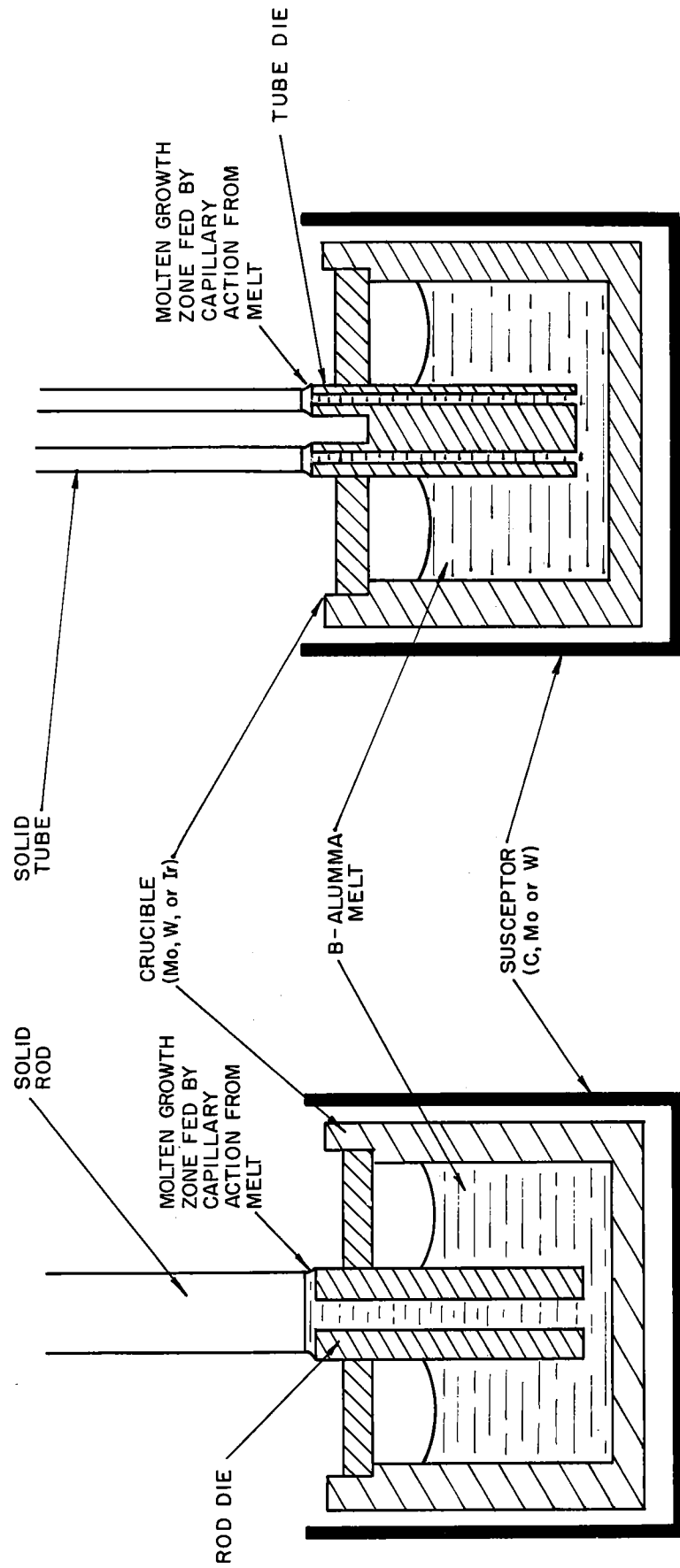


Fig. 2a. Schematic diagram showing crucible and die set-up used for growth of rods

Fig. 2b. Schematic diagram showing crucible and die set-up used for growth of tubes

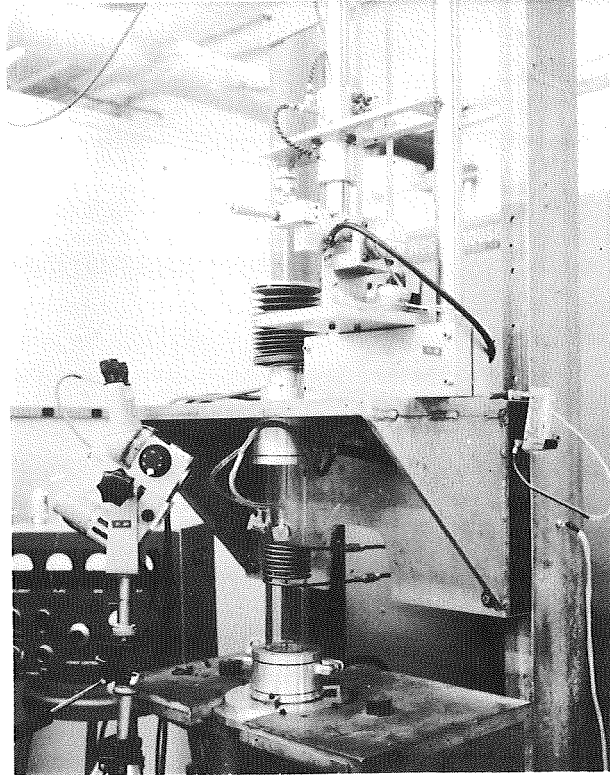


Fig. 3. Crystal growth apparatus

There is a continuing uncertainty with regard to the exact composition of  $\beta$ -alumina. The material commonly obtainable in such form and known as Carborundum Monofrax H  $\beta$ -alumina contains 5.59 wt %  $\text{Na}_2\text{O}$  and is therefore 11.1 =  $\text{Al}_2\text{O}_3$ : $\text{Na}_2\text{O}$  in molar ratio. This material was used for many of the growth experiments. However, Weber and Venero<sup>6</sup> reported the composition of  $\beta$ -alumina as being  $\text{Al}_2\text{O}_3$ : $\text{Na}_2\text{O}$  = 9:1 with a congruent melting point at  $1967^\circ\text{C} \pm 6^\circ\text{C}$ . Both 9:1 and 11:1 molar ratio material were prepared internally. Calculated stoichiometric mixtures of  $\text{Na}_2\text{CO}_3$  and  $\text{Al}_2\text{O}_3$  were mixed and pressed into disks under a pressure of  $\sim 200$  atm. These disks were placed in Pt crucibles and sintered at  $\sim 1150^\circ\text{C}$  for 15 hr under an oxygen atmosphere in a Burrel Box Furnace.

Rods and tubes were grown from  $\beta$ -alumina melt using the experimental technique as described by LaBelle in a recent publication.<sup>3</sup> The crystals grown were examined using optical microscopy in transmitted and reflected light. The composition and occurrence of  $\beta$ -alumina in the crystals grown was determined using standard Debye-Scherrer examination of powdered samples and comparing the pattern and line intensities with standard films. Although the  $\beta$ -alumina pattern is complex and requires sophisticated interpretation, Laue X-ray back reflection photography was used to study the crystallinity of the samples grown.





#### IV. CRYSTAL GROWTH EXPERIMENTS

##### A. Molybdenum Setups

The first growth experiments were carried out using molybdenum components and Carborundum Monofrax H  $\beta$ -alumina as charge material. Three arrangements of the crucible-susceptor were used in experiments aimed at the growth of 0.125 in. diameter rods. These were:

1. Mo crucible, with RF susception directly to crucible
2. Identical Mo crucible inside a larger diameter Mo crucible, with susception to the larger
3. Identical Mo crucible placed inside a graphite cylindrical susceptor in which the RF field was induced.

The modifications outlined above were introduced in order to arrive at the optimum thermal operating conditions, i.e., the minimum melt temperature environment which would allow crystal growth.

$\beta$ -alumina rods were grown from each of the setups at growth rates in the range 2-15 in./hr using a small sliver of Monofrax H, nominally of c-axis orientation as seed. Debye-Scherrer (D/S) examination of a powdered sample taken from the rods revealed that they were mainly  $\beta$ -alumina with an admixture of  $\alpha$ -alumina. Back reflection Laue X-ray photography indicated that some of the rods (or parts) were single crystalline or contained only a few grains. However, the rods were dark, indicating Mo dissolution from the crucible setup, although Mo lines were not observed in the D/S patterns. No chemical analysis was carried out, but visual examination made it apparent that the rods grown from setup no. 3 were nearly translucent and were of the best surface quality.

It was apparent during these experiments that vaporization of sodium or sodium oxide was occurring during growth. It was primarily for this reason that the bellows was introduced at the pulling shaft exit, thus allowing a slight positive

pressure to be maintained within the system. Also, the crucible setup was modified to reduce the exposed surface area of the melt (from which sodium losses will take place) to only the crystal growth area (diameter). This sodium loss is undoubtedly the reason for the appearance of  $\alpha$ -alumina in these and other crystals grown.

A second series of experiments was carried out using Mo components and the growth arrangement involving the graphite susceptor. A Mo tube die was fabricated using rod and tube of matching dimensions. After machining, spacing, and pinning of these basic components, a die which would allow the growth of tubes 0.200 in. o.d.  $\times$  0.160 in. i.d. was available. Charge material of composition  $\text{Al}_2\text{O}_3:\text{Na}_2\text{O} = 9:1$  was used in an effort to compensate for sodium losses. A small single crystal sliver was again used as seed. On bringing the setup to temperature, seeding was successfully carried out and a tube grown at  $\sim 9$  in./hr (sample T1 in Fig. 4). The crucible was emptied and a tube over 2 1/2 in. long was obtained. Approximately 1 1/4 in. of this tube, the last section to be grown, had a smooth surface.

A second growth run was carried out using Carborundum Monofrax H  $\beta$ -alumina ( $\text{Al}_2\text{O}_3:\text{Na}_2\text{O} = 11:1$ ) as charge material. A tube  $\sim 2$  1/4 in. long was grown at about 11 in./hr (sample T2 in Fig. 4).

It was observed that considerable erosion of the Mo die had taken place during both of these growth experiments. However, by mechanical polishing, it was possible to salvage the die for a further growth run. Two changes in the growth procedure were introduced as possible means of reducing the die erosion. It was considered that a possible reason for Mo die erosion during growth was excessive radiant heat from the walls of the crucible. In an attempt to reduce this, a small vertically slotted Mo pipe was placed around the die. The length of the pipe was qualitatively judged so as to produce a temperature gradient that would buffer the excessive radiant heat, yet not reduce the thermal environment by an amount causing difficulty in reaching growth conditions. Secondly, the crucible setup together with the charge was placed in the furnace and flushed with helium overnight to ensure an oxygen and moisture free starting environment. These changes produced no noticeable improvements in either the loss of Na or Mo die erosion. A tube approximately 3 1/2 in. long, which failed to grow entirely cylindrical, was grown.

D/S X-ray diffraction patterns confirmed that samples taken from the beginning, middle, and end of sample T1 were  $\beta$ -alumina, containing  $\alpha$ -alumina as a second phase. Comparing line intensities with D/S patterns taken from rods, it appeared that there was more  $\alpha$ -alumina present and that it increased as the growth of the tube progressed.

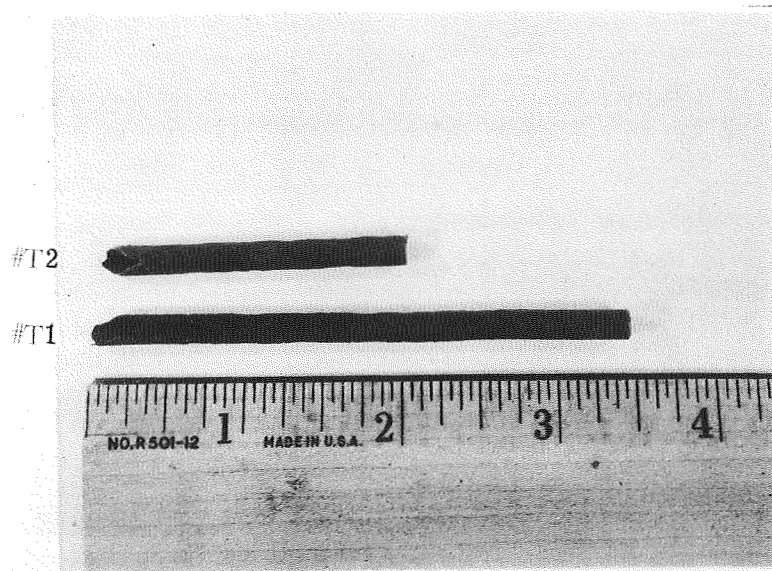


Fig. 4.  $\beta$ -alumina tubes grown at 8 to 11 in./hr using molybdenum setups

## B. Tungsten Setups

Experience with the growth of  $\alpha$ -alumina (sapphire) has shown that tungsten components are thermodynamically more compatible. It was decided to check if this was also true for  $\beta$ -alumina in an effort to reduce crucible and die dissolution and later precipitation during crystal growth.

A complete growth setup was fabricated from tungsten (i.e., crucible and die). This proved to be a complex procedure due to the brittleness of tungsten, which makes machining slow and difficult. Acid etching in HF:HNO<sub>3</sub> = 1:1 proved to be the only successful means of producing the thin walled parts of the die. The basic components were then spaced and pinned to produce a W die which would allow the growth of tubes 0.250-in. i.d.  $\times$  0.200-in. o.d. A Mo susceptor was used.

Carborundum Monofrax H  $\beta$ -alumina was used as charge material and a small single crystal sliver of the same material served as a seed. Thermal growth conditions proved to be more difficult to achieve with W than with the Mo components. This is probably related to the higher thermal conductivity of W,  $\sim 1 \text{ W/cm}^2$ , compared with  $\sim 0.65 \text{ W/cm}^2$  for Mo, at 2000 °C. This means that the melt temperature has to be raised to compensate for increased radiation losses. A small, dark colored tube was grown which proved to be almost entirely  $\alpha$ -alumina. Also, the walls of the tungsten crucible had been excessively attacked, possibly worse than with Mo components.

It was concluded that W components could not be used, and that Ir was the next logical choice.

## C. Iridium Growth Setup

$\beta$ -alumina rods were grown from an iridium crucible and die setup. The latter proved to be compatible with the melt material, no metallographically detectable erosion taking place.

A 0.625 in. diameter iridium crucible was used. The bottom end of the 0.125 in. diameter Ir rod die was pressed into an Ir disk which could be located at the bottom of the crucible, thus maintaining the die in a vertical position. This method of mounting the die was used because the components normally involved were not available in iridium and machining would have been costly. However, it is not the most efficient setup design. In particular, it is unfavorable from the point of view of creating a growth thermal environment at a low RF power setting.

Two growth runs using Carborundum Monofrax H  $\beta$ -alumina as charge material and a small sliver as seed were carried out. During the second run, after introducing heat shielding modifications, a rod about 2 in. long was grown. A piece of material taken from the center of this rod was crushed and used to obtain a D/S pattern. A mixture of  $\beta$ - and  $\alpha$ -alumina was detected. The  $\beta$ -lines were more intense (relative to the  $\alpha$ -lines) than with the samples grown from the Mo setups. It was noted that during growth considerably less "smoking" was observed, despite the more open nature of the growth setup and the higher heat input required to produce the necessary growth conditions. Also examination of the setup after growth indicated that no attack of the crucible or die had occurred. After growth, the melt material remaining was a very pale blue color, due perhaps to back streaming of Mo from the radiation-shielding.

Slices were cut out of the rod grown perpendicular to the growth direction and just above the region used to obtain the D/S patterns. Five of these slices were mounted and polished using standard metallographic techniques to  $\sim 0.004$  in. thick.

Between cross polarizers in transmitted light, the slice exhibited a two-phase distribution, taking up three-fold symmetry (Fig. 5). This was at first thought to be the (0001) plane but, on rotation about the growth axis, the minority phase exhibiting the three-fold symmetry was found to extinguish every  $90^\circ$ . Using reflected light, the same symmetry distribution was observed. It is evident that the phase proportions are about 60:40, although it is not possible to separate them into  $\alpha$  and  $\beta$  at this time. Using unpolarized light, the polished slices appeared as in Fig. 6 with no obvious sign of symmetry. These micrographs confirm the D/S evidence of the two phase nature of the rods.

Laué back reflection photographs taken from similar slices approximately parallel to the growth direction are typical of single crystals and show no evidence of the spot splitting which might be expected from a two-phase sample (Fig. 7). This implies that the phases are oriented in the same direction. The Laué photograph shows three-fold symmetry and was confirmed as being the  $(10\bar{1}1)$  plane found in  $\alpha$ -alumina. Thus, it appears that the  $\beta$ -alumina is oriented with respect to the  $\alpha$ -alumina structure. An example of the true  $\beta$ -alumina symmetry was obtained by taking a Laué from a Monofrax H  $\beta$ -alumina sliver platelet. The platelet was X-rayed on a flat face perpendicular to the growth plane used, and the photograph is shown in Fig. 8. The crystal face X-rayed is the (0001) plane of  $\beta$ -alumina and

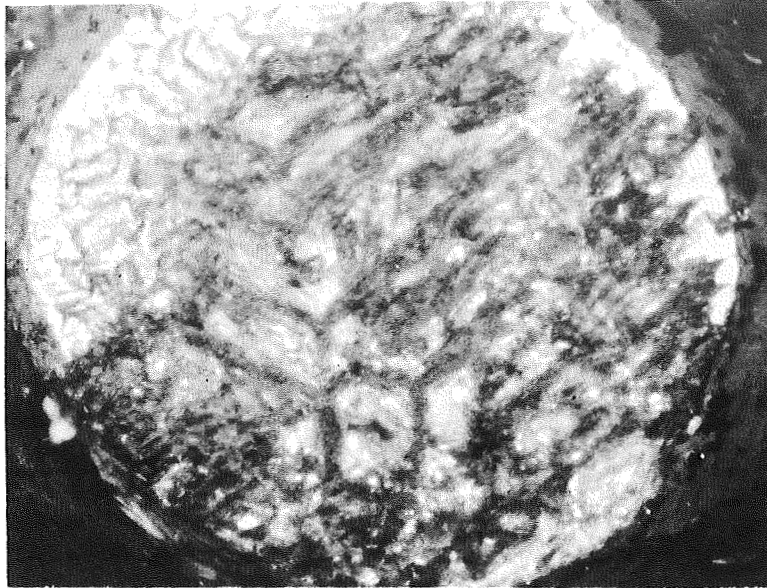


Fig. 5.  $\beta$ - $\text{Al}_2\text{O}_3$  rod grown from iridium setup (viewed parallel to growth direction in polarized reflected light at 75X)

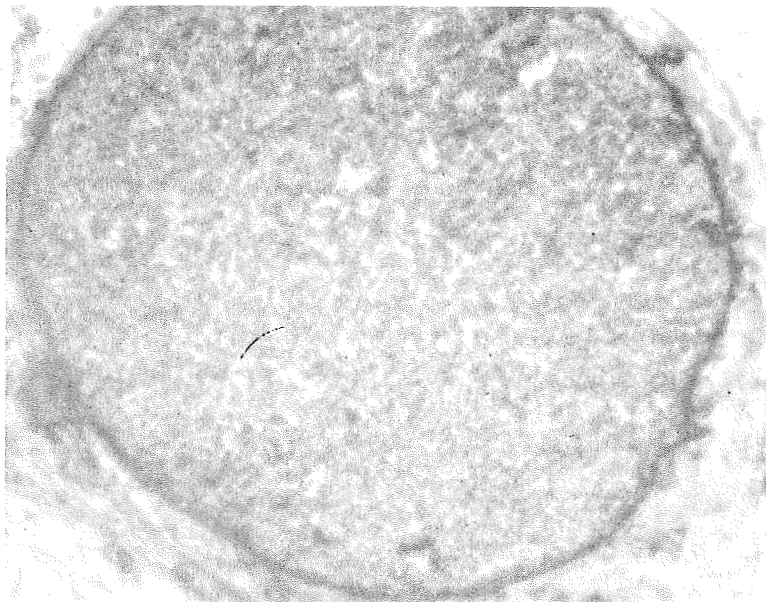


Fig. 6.  $\beta$ - $\text{Al}_2\text{O}_3$  rod grown from iridium setup (viewed parallel to growth direction in reflected light at 75X)

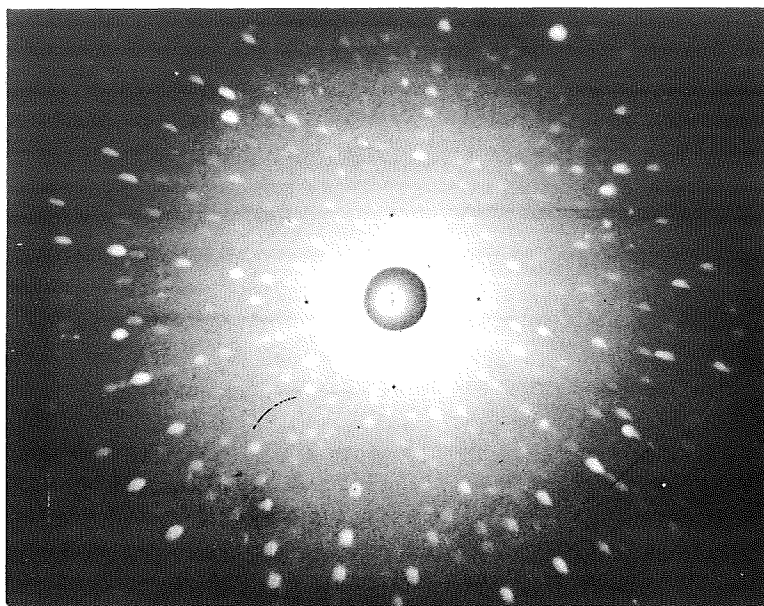


Fig. 7. Laue back reflection photograph of area shown in Figs. 4 and 5 [ $\{10\bar{1}1\}$  plane in  $\alpha$ - $\text{Al}_2\text{O}_3$ ]

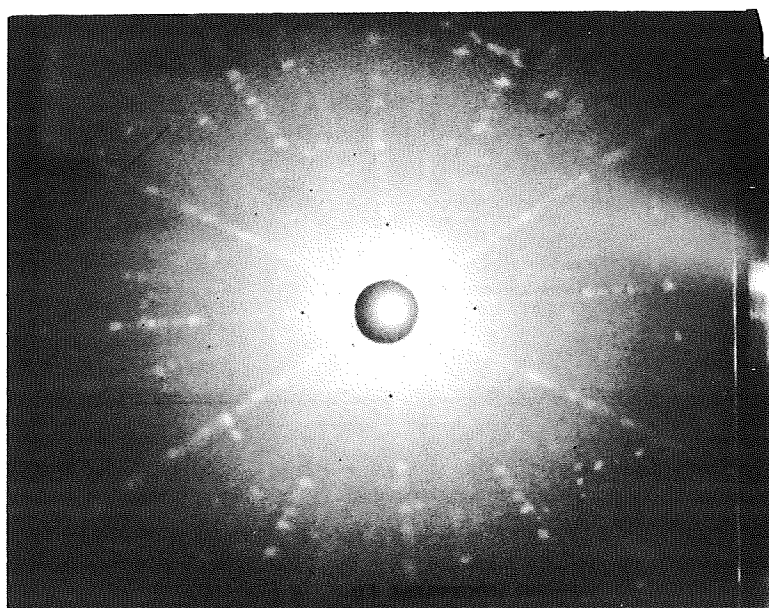


Fig. 8. Laue back reflection photograph of flat surface of Monofrax H  $\beta$ - $\text{Al}_2\text{O}_3$  sliver platelet shows  $\{0001\}$  plane of hexagonal  $\beta$ - $\text{Al}_2\text{O}_3$  (long axis of sliver runs from top to bottom)



hexagonal six-fold symmetry with six mirror planes is evident. By contrast, the (0001) plane of  $\alpha$ -alumina exhibits three-fold symmetry with three mirror planes.

The Laue' photographs from the platelets are fuzzy compared to the photographs obtained from the rod, even though a "single crystal" was used. An a-axis Laue' could not be obtained from the platelets due to this excessive splitting.

The  $(10\bar{1}1)$  orientation of the rod grown, which is  $18^\circ$  from the axis of the seed platelet, is probably due to a magnification of an original misalignment.

## V. CONCLUSIONS

It has been demonstrated that melt growth of  $\beta$ -alumina sheaths using a novel crystal growth technique developed by Tyco Laboratories, Inc. is feasible. Tube and rods containing mixtures of  $\beta$ - and  $\alpha$ -alumina have been grown from components fabricated from Mo, W, and Ir. It is concluded that, in regard to thermodynamic compatibility with the  $\beta$ -alumina melt, only iridium components may be used without excessive erosion and dissolution of the crucible and die material in the melt. Rods grown using Ir setups were two phase, yet exhibited single crystallinity, indicating that the phases were mutually oriented with respect to each other.

The major problem remaining to be solved is loss of sodium by volatilization from the melt during growth. This is undoubtedly the reason for the appearance of  $\alpha$ -alumina in the samples grown. It is suggested that a furnace be constructed such that the  $\beta$ -alumina tubes may be grown under inert gas pressures of up to 30 atm, since it has been demonstrated by other research that this is a suitable method for suppressing the loss of volatile components during melt growth.

It is possible that, if the ionic conductivity of the  $\beta$ -phase in the two-phase structure is that of the stoichiometric single crystal, some advantages in mechanical strength might accrue from the use of two-phase membranes. Also, control of the alpha content could result in a material which would have value as a "graded seal" to pure alumina, and have potential use in practical battery systems.



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APPENDIX

REPRINTS OF PUBLICATIONS DESCRIBING  
EDGE-DEFINED, FILM-FED GROWTH



GROWTH OF CONTROLLED PROFILE CRYSTALS FROM THE MELT:  
PART I - SAPPHIRE FILAMENTS

H. E. LaBelle, Jr. and A. I. Mlavsky  
Tyco Laboratories, Inc.  
Waltham, Massachusetts 02154

(Received May 27, 1971; Communicated by J. B. Goodenough)

ABSTRACT

A crystal growth technique is described in which a tubular, annular, or ribbon-shaped capillary orifice is used to maintain the liquid level constant during growth and to determine the shape of the growing crystal. The orifice material must be wetted by, but chemically nonreactive to the molten phase of the crystal to be grown. Using molybdenum orifices and crucibles, single crystal sapphire filaments several hundred feet in length and diameters of .01 - .05 cm have been grown at speeds of 2.5 - 5 cm/min; c-axis crystals have been grown at rates up to 20 cm/min, and a variety of other crystal orientations has been grown at speeds up to 2.5 cm/min. Sapphire tubes, ribbons and multiple filaments have also been grown.

Over the past several years, we have been concerned with the development of techniques for the continuous growth of controlled profile single crystals from the melt. During the course of this work, a succession of techniques has been developed such that we are now able to grow essentially continuous crystals (several hundred feet long in the case of filament) of almost arbitrarily controlled cross section directly from the melt. The techniques have mostly been applied to the growth of  $\alpha$ -alumina although other materials including spinels, titanates, other oxides, metals, and ionic salts have also been grown.

In Part I of this series, we describe the basic technique by which continuous sapphire filaments have been grown and we indicate the applicability of the method to the growth of other materials and other shapes. In



Part II, \* one of us (H. E. LaB.) describes a refinement of the technique which greatly aids in the accurate control of the dimensions of the growing crystal and which enhances a self-stabilizing feature of the growth. In Part III, the basic theory of that method is described, including a discussion of the effect of the growth process on the morphology of filaments, particularly of  $\alpha$ -alumina. In Part IV, detailed experimental results on the growth morphology are reported and compared with the theoretical predictions.

### Part I: Sapphire Filaments

Techniques for the continuous melt growth of filaments have been previously reported. Thus, von Gomperz (1) grew metal filaments, Gaule and Pastore (2) grew germanium, and LaBelle and Mlavsky (3) reported the growth of sapphire filaments. In all of these approaches, the crystal was pulled through a disc-like die located on the surface of the melt. The technique described here requires the use of a rigid capillary made from a material that is wetted by, but nonreactive to the molten phase of the crystal to be grown. Use of the technique permits the growth of single crystal sapphire filaments in lengths of hundreds of feet; ribbons, tubes and other shapes are also grown by a slight variation of the technique which has also been applied to the growth of materials other than  $\alpha$ -alumina.

### Basic Approach

Previously we described a "floating orifice technique" (4) by which sapphire filaments of reasonably controlled geometry were grown from the melt. The orifice was fabricated from molybdenum which is wetted by the melt and which "floats" on the surface thereof. A disadvantage of this technique in the preparation of continuous filaments arises from the fact that the floating orifice continuously lowers as the filament is grown and the melt depleted. Also, a rather elaborate temperature control is required for continuous growth over an extended period.

In the present technique (5), a capillary tube (typically fabricated from molybdenum) is attached to the bottom of a crucible (also molybdenum) in such a way that liquid is able to enter the bottom of the capillary. Because the contact angle,  $\theta$ , of molten alumina is less than  $90^\circ$ , liquid rises in the capillary an amount,  $h$  cm, given by:

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\* "Growth of Controlled Profile Crystals From the Melt," Parts I, II, III, and IV will be published in this Journal.

$$h = 2\gamma \cos \theta / \rho r g$$

where  $\gamma$  is the surface tension, dyne/cm,  $\rho$  is the density of the melt, gm/cm<sup>3</sup>,  $r$  is the tube radius, cm, and  $g$  is the acceleration due to gravity, 981 dyne/cm.

Reported values for the surface tension of molten alumina range from  $360 \pm 40$  dyne/cm from meniscus measurements made in molybdenum to  $638 \pm 100$  dyne/cm from meniscus measurements made in tungsten (6). Our observations of capillary rise in molybdenum tubes indicate a somewhat higher value, but in any event a rise of several centimeters is observed in tubes of up to a millimeter in inside diameter.

Fig. 1 shows the case where the height of the top of the capillary above the liquid level in the crucible goes from  $h_1$  to  $h_2$  as the crucible empties. Clearly, so long as  $h_2$  is less than  $h$  where  $h = 2\gamma \cos \theta / \rho r g$ , the liquid level will remain at the top of the capillary until the crucible is completely emptied. Accordingly, the use of a capillary arrangement of the kind shown in Fig. 1 provides a technique for maintaining a constant liquid level for filament growth as the melt is consumed. This introduces a considerable element of thermal and mechanical stability compared to techniques that use, for example, floating orifices which change position during the growth process.

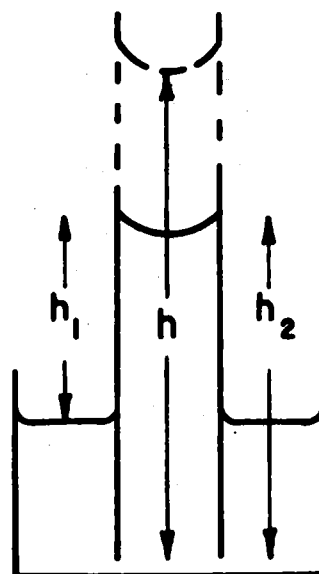


FIG. 1

$$h_2 < h = 2\gamma \cos \theta / \rho r g$$

In Fig. 2 the actual growth process is depicted. The temperature at the top of the capillary is arranged to be close to the melting point and an  $\alpha$ -alumina seed crystal of the desired orientation is dipped into the melt at the top of the capillary. As the seed crystal is pulled, the curvature shown in Fig. 2 at the solid-liquid interface is increased, with a consequent reduction in pressure within the liquid by an amount  $\Delta p$  given by:

$$\Delta p = \gamma (1/r_1 - 1/r_2)$$

If the temperature conditions are adjusted appropriately, the filament will solidify at the rate at which it is being pulled, maintaining an essentially constant  $\Delta p$  to continue the supply of liquid.

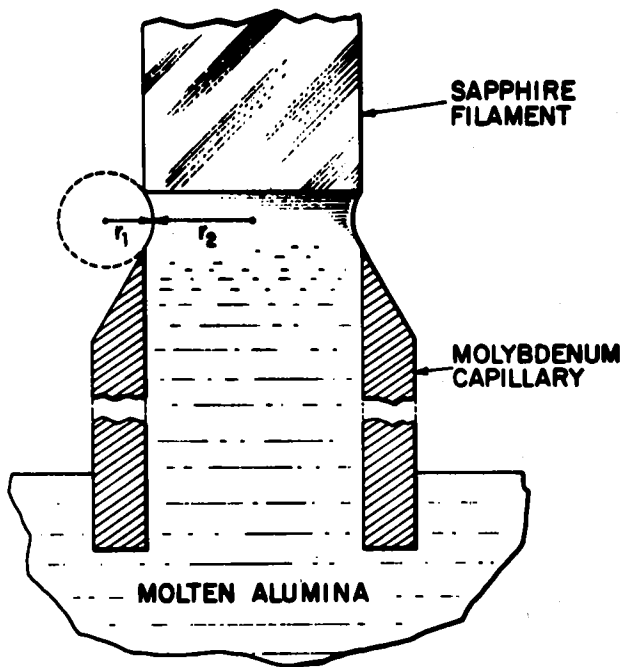


FIG. 2  
The growth process

In Fig. 3(a), an arrangement for the growth of sapphire tubing is shown wherein the single capillary used for filament is replaced by two molybdenum tubes which are arranged so as to create a cylindrical liquid reservoir. Fig. 3(b) shows a simple arrangement of two parallel molybdenum plates from which sapphire ribbon can be grown.

#### Apparatus

Since the technique, with the exception of the capillary mounted with-

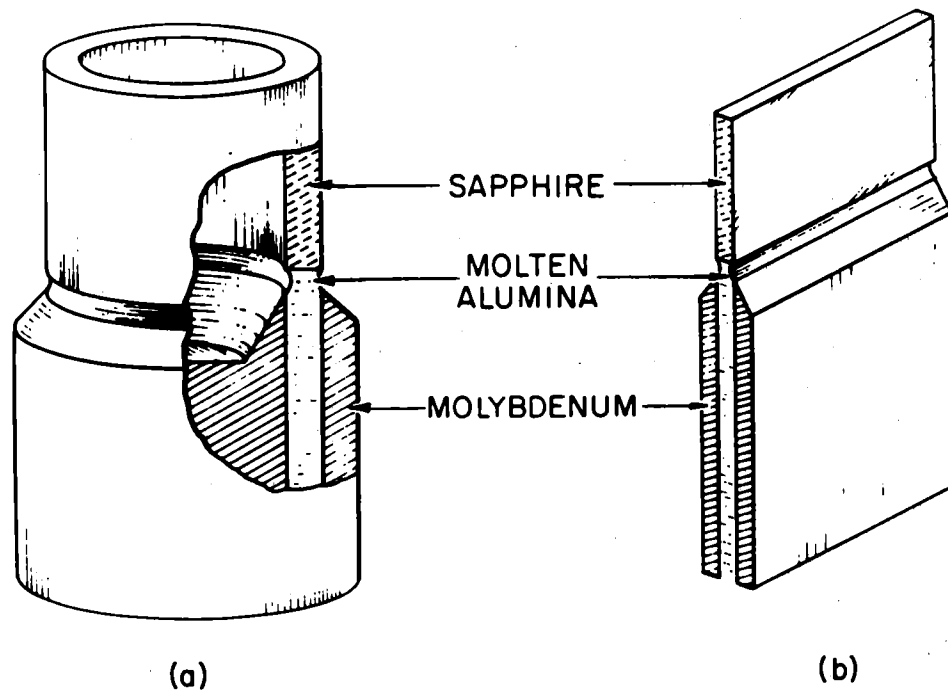


FIG. 3  
Growth from the melt of a) sapphire tube, b) sapphire ribbon

in the crucible, is essentially identical to Czochralski growth, any standard melt growth furnace can be used. The pulling mechanism, however, may require modification especially to enable the growth and spooling of continuous filaments.

The specific apparatus we have used for most of our experiments is shown diagrammatically in Fig. 4. The molybdenum capillary assembly is supported in a molybdenum crucible which is used to contain the melt. The crucible is positioned in a double jacketed, water cooled quartz chamber and heated by RF of 450 KHz from a 20 kw generator. The inside of the tube is maintained in a helium or argon atmosphere.

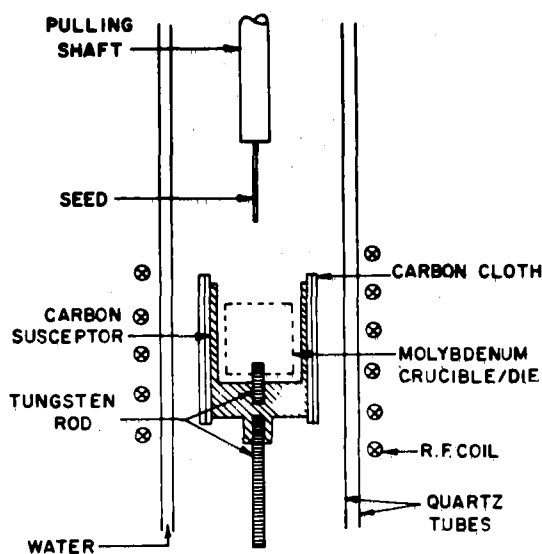


FIG. 4

Crystal growth apparatus

For the growth of ribbons, tubes, and other stiff shapes of limited lengths, the pulling motion is imparted by a moving platen; two motor-driven endless belts, between which a filament is sandwiched, are used for continuous growth. The filament is collected on a spool operated by a slipping clutch.

For most of the experiments, molybdenum has been used since it has good compatibility with molten alumina, low cost and easy machinability. Tungsten has also been used successfully and we assume that iridium would be suitable although its high cost and poor machinability make it an unattractive candidate.

### Experimental Results

The main purpose of this part of the investigation was to develop a process for the continuous preparation of single crystal sapphire filaments primarily for use in structural composites. A secondary goal was to investigate the applicability of the method to the growth of other sapphire shapes. A successful filamentary reinforcement must combine high tensile strength and modulus with good uniformity and low cost. Accordingly, the emphasis on the experiments to be reported below was on determining the fastest rate

at which it was possible to grow continuously sapphire filament with the *c*-direction along the axis of growth since it is in this direction that sapphire exhibits the maximum value of modulus of elasticity. We had also previously shown (3) that dendrites in sapphire are spontaneously propagated in the *c*-direction which indicated that this might also be the direction in which the fastest growth rate might be achieved.

The apparatus shown in Fig. 4 was used to establish the conditions for filament formation by trial and error. Thus the temperature at the top of the capillary was adjusted to be close to the melting point, a *c*-axis seed was lowered to contact the melt and then withdrawn while making appropriate adjustments in speed and temperature to maintain a predetermined filament diameter. During the course of such experiments, it was observed that the system displayed a considerable degree of self-stabilization in the sense that filament of a fairly constant diameter could be grown over a range of temperatures and pulling rates. Accordingly a series of experiments was performed to determine quantitatively, as a function of growth rate, the temperature variation that the system could accommodate for growth at a more or less constant diameter filament.

For these experiments, two tubes were mounted symmetrically in the same crucible; one of the tubes had an .025-cm orifice for filament growth, and the other an .15-cm orifice to accept a tungsten-rhenium thermocouple. Experiments were then run in the following manner: The temperature was brought up to the melting point, a *c*-axis seed was inserted, held for 1 min in the melt, and then withdrawn at a constant speed. The temperature as measured by the thermocouple was recorded initially as 2040°C although the actual melting point of alumina is reported as 2050°C. After about 5 cm of filament had been grown, the temperature was increased and recorded at the point where the filament pulled free from the melt. The melt was then cooled back down to an indicated value of 2040°C and the process repeated using a sequence of growth speeds. The data so obtained are shown in Fig. 5, from which it can be seen that there exists a systematic relationship between the pullout temperature and the growth speed, the filaments grown at slower speeds continuing to grow over a wider temperature range than those grown at faster speeds. This clearly implies that it is desirable to grow at a rate less than the possible maximum when growing continuously, so that minor temperature fluctuations do not interrupt growth.

Growth speeds of up to 20 cm/min have been achieved with pre-

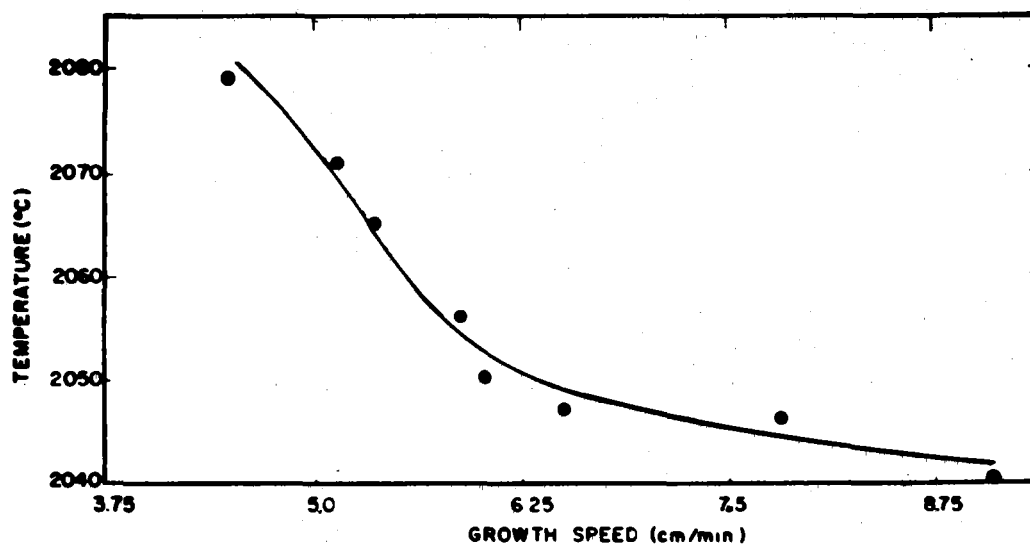


FIG. 5

Dependence of pullout temperature on growth speed for  
.025-cm-diameter filament

chosen filament diameters in the range .01 - .05 cm; however, good diameter control over a long period required that the rate be 2.5 - 5 cm/min. Although most of our work involved growth in the *c*-direction, we have been able to grow continuous sapphire filaments in essentially any crystallographic direction so long as the rate of growth is kept to about 2.5 cm/min or lower. At faster speeds where dendritic growth is apparently occurring, the *c*-axis is the preferred one for continuous filament propagation. This, as we noted above, is the major dendritic direction for sapphire. In Fig. 6, an example of a *c*-axis sapphire filament is shown; Laue back-reflection analysis of the filament shows it to be a single crystal with a small number of low angle grain boundaries. Filaments such as this exhibit average tensile strengths greater than 300,000 psi (using a 2.5-cm gauge length, and a strain rate of  $.005 \text{ min}^{-1}$ ) and a modulus of elasticity  $67.5 \times 10^6 \text{ psi}$ . (7)

Using the die designs shown in Fig. 3(a) and 3(b), sapphire tubes and ribbons have been grown respectively. In all cases, the precise shape of the growing crystal is determined by the shape of the liquid reservoir formed at the top of the die. Tubes of typically a 1 cm outside diameter and an .075-cm wall thickness have been grown at rates up to 3.5 cm/min; ribbons up to 2.5 cm wide and typically .075-cm thickness have been grown at similar rates.

These results indicated that the use of a capillary feed arrangement

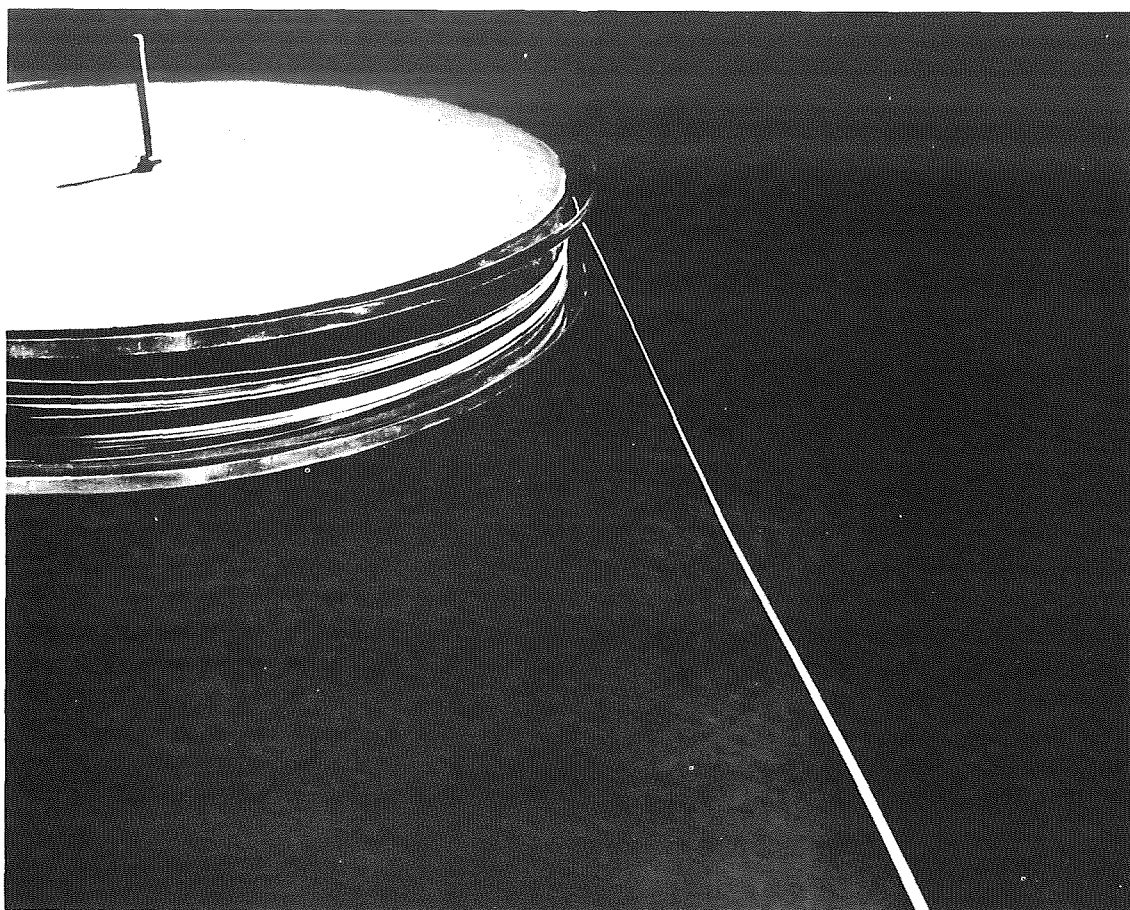


FIG. 6

Photograph of sapphire filament

to maintain a constant liquid level for growth independent of the liquid level in the crucible and to control the shape and size of the growing crystal lends itself also to the growth of several sapphire crystals simultaneously. We have experimentally confirmed this prognostication by growing three filaments simultaneously from a single crucible using three capillary assemblies placed radially symmetrically and using three separate seeds mounted on a common pulling shaft.

In Part II of this series, an improved version of this crystal growth technique is described which extends the process to the growth of virtually any chosen cross-sectional shape from the melt.

#### Acknowledgments

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due to Mr. John Bailey and Mr. William Little who aided in the experiments, and to Dr. George Hurley who made mechanical measurements on the crystals.

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GROWTH OF CONTROLLED PROFILE CRYSTALS  
FROM THE MELT: PART II - EDGE-DEFINED,  
FILM-FED GROWTH (EFG)

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ABSTRACT

A crystal growth technique is described, "Edge-Defined, Film-Fed Growth" (EFG), by which continuous single crystals having virtually any cross-sectional shape can be grown from the melt. Crystals with shapes ranging from simple rods or filaments to almost arbitrarily complex cross sections may be grown with excellent dimensional control over very long lengths with minimal temperature and speed control. The EFG technique is an extension of that described in "Growth of Controlled Profile Crystals from the Melt: Part I"\* in that a capillary structure is used to furnish a constant liquid level at the growth interface as melt in the crucible is depleted. In the present technique, however, the shape of the growing crystal is determined by a thin melt layer sandwiched between the growing solid liquid interface and the plane top surface of the rigid capillary structure. The crystal grows only over solid regions of the die surface and not over any deep depressions in this surface. Accordingly any pattern of depressions fabricated into the top surface of the die will be propagated in the growing crystal. In this paper the application of the process to the growth of various single crystal sapphire shapes directly from the melt is described.

Process Description

In Fig. 1(a), a system is shown comprising a supply of liquid in a container, a solid capillary tube mounted vertically in the liquid and connect-

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\* "Growth of Controlled Profile Crystals from the Melt," Parts I, II, III, and IV will be published in this Journal.

ing to the liquid supply, a thin film of liquid on the top plane surface of the capillary, and a solid rod connecting with the upper surface of the liquid film. A necessary requirement for achieving this arrangement is that the liquid wet both the capillary and the upper solid. The conditions for stability in such a system will be described in detail in Part III; however, suffice it to say that the liquid will not run over the edge of the capillary since, if it did so, a perpetual motion device would result. The hydrostatic pressure,  $\Delta p$ , in the film is given by:

$$\Delta p = \gamma (1/r_1 - 1/r_2)$$

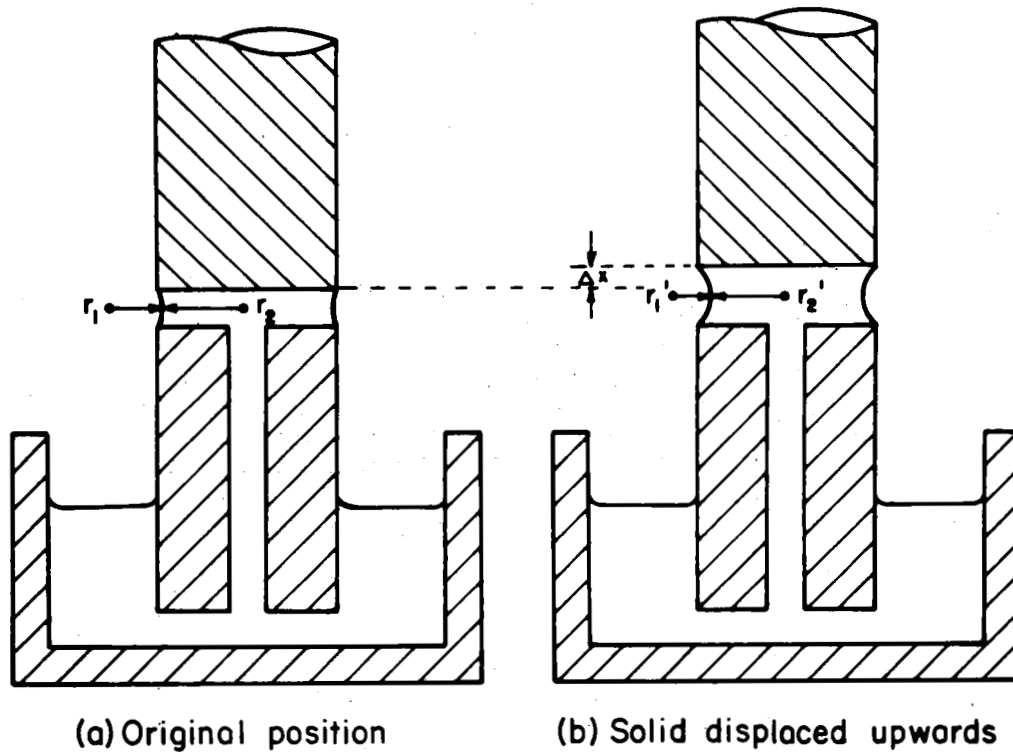


FIG. 1

Model system

This differs from atmospheric pressure by the "head" of liquid in the capillary. In Fig. 1(b), we consider that the solid rod is instantaneously displaced upward by an amount  $\Delta x$ , producing a bowing in of the liquid (since mass is conserved) so that  $r_1$  becomes  $r_1'$  and  $r_2$  becomes  $r_2'$  (where  $r_2' \approx r_2$ ). It can readily be seen that the hydrostatic pressure in the film, now  $\Delta p'$  given by

$$\Delta p' = \gamma (1/r_1' - 1/r_2')$$

is such that  $\Delta p' > \Delta p$ . As a result, additional liquid is sucked up into the film from the reservoir below.

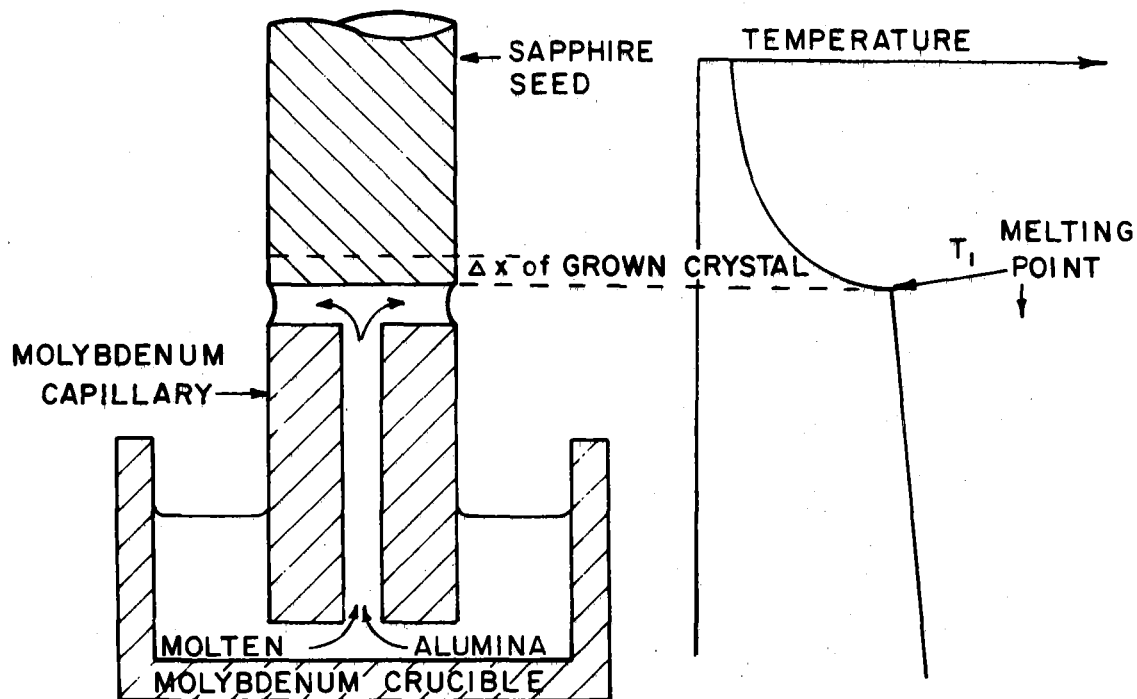


FIG. 2

Sapphire rod growth by EFG

In Fig. 2, a specific system is shown wherein the container and the capillary are molybdenum, the upper solid is a sapphire rod, and the liquid is molten alumina (wets both solids). Again consider that the sapphire rod is instantaneously displaced upward by an amount  $\Delta x$  with a consequent reduction of the hydrostatic pressure in the film. While molten alumina flows upward through the capillary to equilibrate the pressure difference, the temperature distribution in the system is such that the solid grows downward at the expense of the liquid an amount  $\Delta x$  to the level of the original solid liquid interface. Under steady state conditions, the solid rod is pulled upward at some constant rate, with solidification proceeding downward at the same rate. This technique (1) permits the growth of a crystal from a molten film sandwiched between the growing crystal and a die, the shape of the crystal being defined by the external rather than the internal shape of the die.

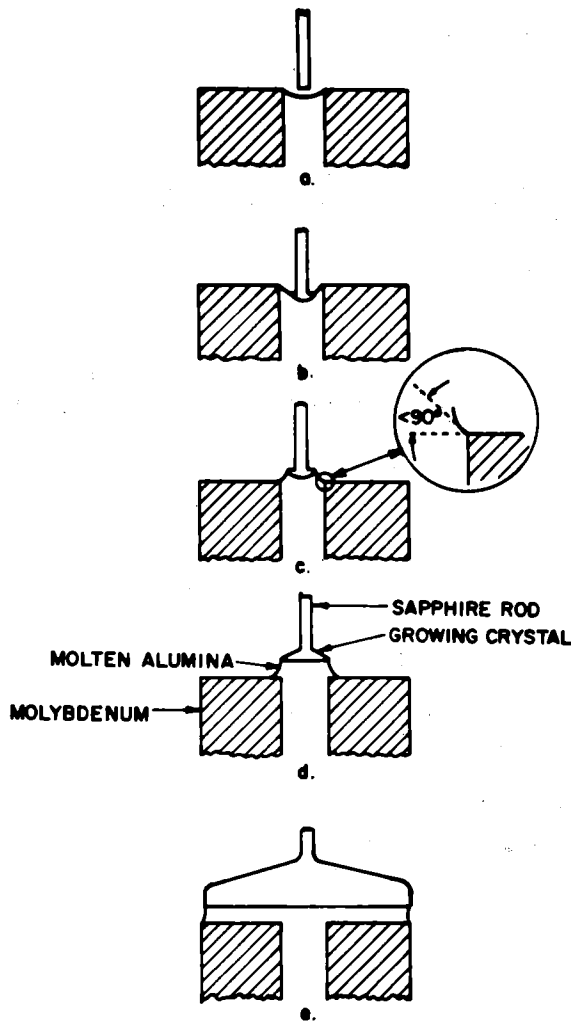


FIG. 3

Development of shape  
from seed crystal

In Fig. 3 is shown the sequence of stages by which the situation described in Fig. 2 is arrived at. As described in "Growth of Controlled Profile Crystals from the Melt: Part I," a capillary is supported in a supply of the molten material, the dimensions being such that liquid rises to the top of the capillary regardless of the liquid level in the crucible. As shown in Fig. 3(b), a small diameter seed crystal (of the desired crystallographic orientation) is inserted into the orifice and the temperature is adjusted so that material solidifies onto it. As the seed is withdrawn and the melt is pulled up above the surface of the die, liquid begins to spread across the die since the contact angle is less than  $90^\circ$ . When the liquid reaches the edge of the die, however, as shown in Fig. 3(c), the liquid ceases to advance. The crystal will now continue to grow with the diameter determined by

the outside diameter of the die as shown in Fig. 2

The liquid will spread across the top surface of a die until it reaches any vertical (or nearly vertical) plane surface where it stops. Since the liquid has no way of discriminating between an outside and an inside edge, a continuous hole may be grown into the crystal if a blank hole is drilled into the top surface of the die (Fig. 4). There will, however, be a minimum diameter below which surface tension causes the film around the hole to fill in. The quantitative limits of the technique are discussed below for a number of simple shapes. These tend to set minimum rather than maximum dimensions for the profile of crystals that can be grown. There is clearly

no limit to the complexity of the profile (see for example, Fig. 5), but only to the smallest radii of curvature that form part of the pattern. Further by reference to the discussion accompanying Fig. 3, it can readily be seen that crystals of arbitrary complexity can be grown using the simplest seed geometry, namely a small diameter rod.

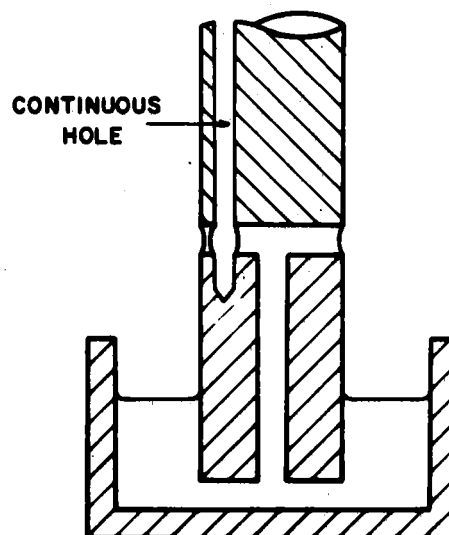


FIG. 4

Rod with continuous eccentric hole

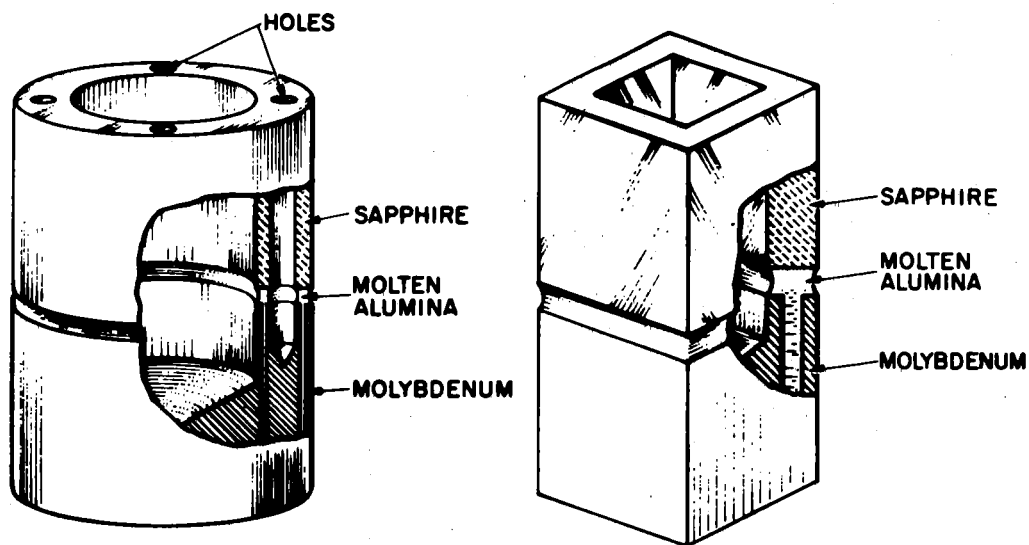


FIG. 5

Complex shapes

Since the shape of the growing crystal is defined by the edge of a die and growth takes place from a film of liquid which is continuously replenished, the denotative name "edge-defined, film-fed growth" (EFG)\* has

\* Name suggested by A. I. Mlavsky.

been given to the technique. The process is described here in qualitative terms; a more detailed basic theory of the process including a discussion of the limits of stability of the system will be presented in Part III of this series.

### Apparatus

The apparatus used for EFG is essentially a modified Czochralski unit as previously described in Part I of this series. The majority of all sapphire crystals has been grown from a molybdenum crucible in an argon atmosphere. Alternates such as tungsten and iridium crucibles and a helium atmosphere may also be used.

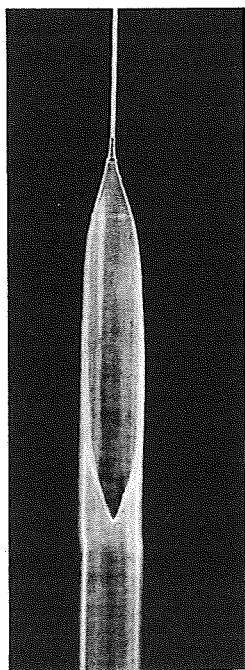


FIG. 6

Development of tube  
from rod seed

### Experimental Results

In a typical experiment, a molybdenum crucible is provided with a molybdenum die of a chosen configuration, charged with small particles of  $\alpha$ -alumina and heated by means of RF in the equipment previously described. An approximate estimate of the correct conditions for growth is afforded by observation of molten alumina rising to the top of the capillary orifices within the die. A small diameter preoriented sapphire seed is lowered to contact the melt in one of the orifices. The seed is then moved upwards, and the speed and/or temperature are adjusted so that the liquid spreads out across the surface of the die to form the complete profile that it is intended to grow. In practice, the desired cross-sectional shape is achieved within 2 - 5 cm of growth as shown in Fig. 6.

Using EFG by the method indicated above, sapphire filaments, ribbons, and tubes are being grown. In Fig. 7, a variety of sapphire shapes is shown. In Table 1, the maximum and minimum sizes grown in various simple shapes is summarized. Filaments have been grown in lengths up to several hundreds of feet since they are flexible and readily lend themselves to continuous collection on a spooling mechanism; inflexible shapes such as tubes have been grown in lengths up to 5 feet. For accurate control of diameter, the maximum growth rate for filaments,

TABLE 1

## Sapphire Shapes Produced

| Shape    | Length<br>(maximum, cm) | Dimensions    |               |
|----------|-------------------------|---------------|---------------|
|          |                         | (maximum, cm) | (minimum, cm) |
| Filament | 11,500                  | .5 diameter   | .013 diameter |
| Tube     | 150                     | 2.5 o.d.      | .05 o.d.      |
|          |                         | 2.35 i.d.     | .025 i.d.     |
| Ribbon   | 150                     | 2.5 wide      | .1 wide       |
|          |                         | .15 thick     | .008 thick    |

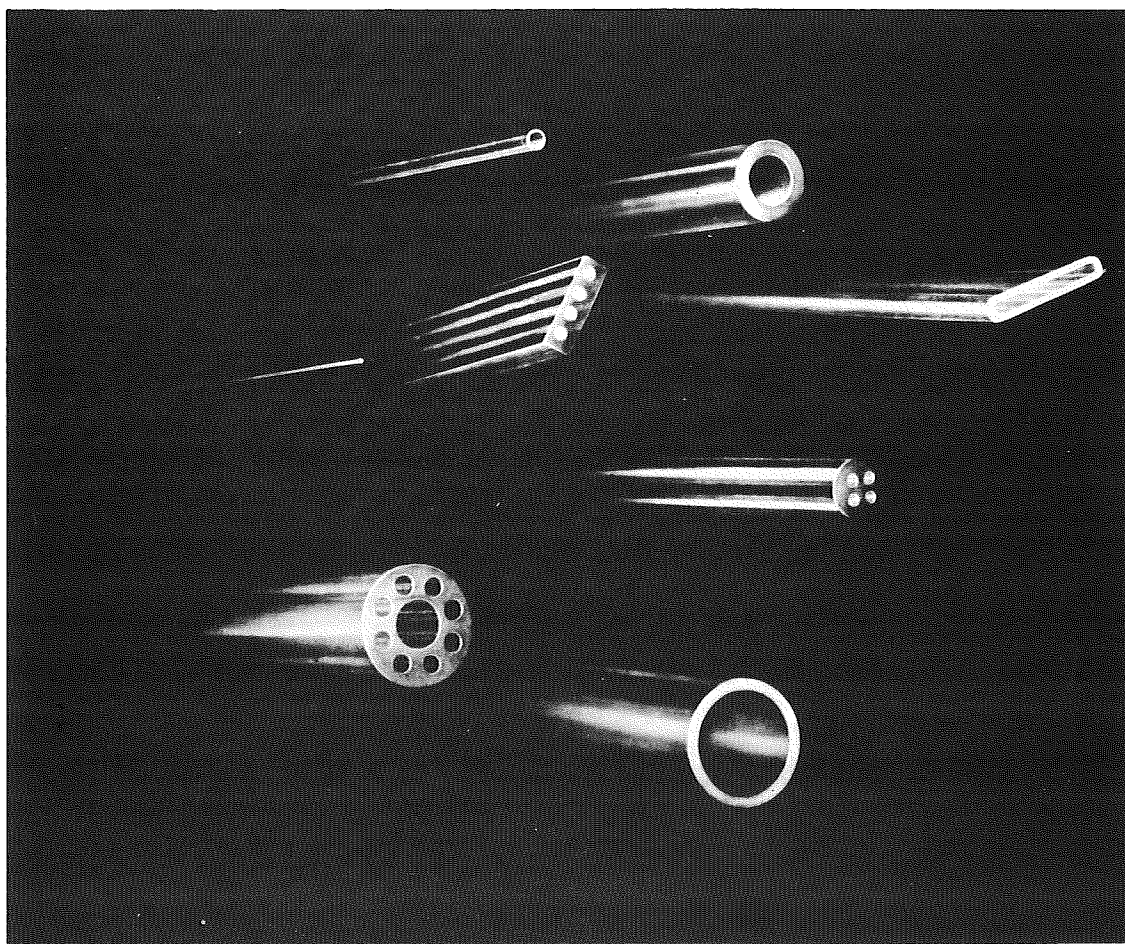


FIG. 7

Sapphire shapes produced directly from the melt by EFG.



typically .025-cm diameter is 5 cm/min. As the cross section gets larger, this rate is reduced; for example, the maximum rate of growth for a tube 1.0-cm o.d. x .075-cm wall thickness is approximately 2 cm/min. It is clear that, to grow filaments several hundred feet in length, growth must be continuous over periods of days. The self-stabilizing features of the technique which make it possible to achieve growth from the melt over such very long periods without the necessity for accurate temperature control are described in detail in Part III of this series.

The micromorphology of sapphire produced by this technique will be discussed in detail in Part IV of this series. Briefly, the micromorphology consists of an array of microvoids which vary in size and number depending on the actual growth conditions. Fig. 8 shows two filament cross sections viewed under transmitted light. The filament shown in Fig. 8(a) was grown at 5 cm/min while that shown in Fig. 8(b) was grown at 1.3 cm/min. This type of microvoid distribution is observed in all sapphire filaments grown at relatively fast speeds by EFG, with the specific exception of totally clear filament (2) grown under certain conditions to be described in Part III.

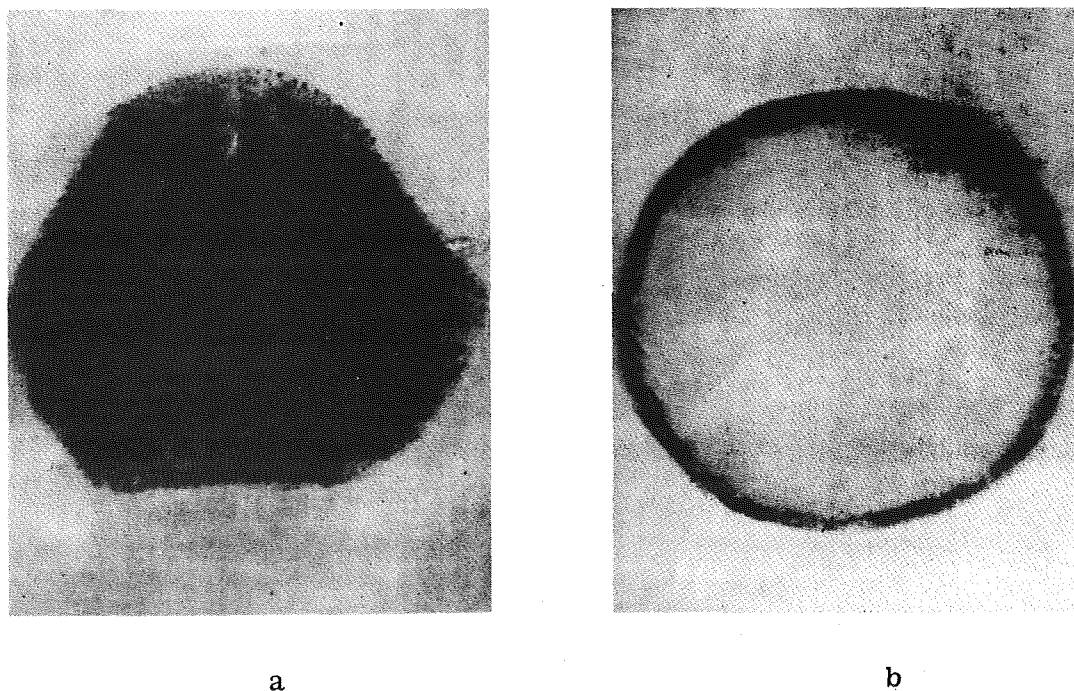


FIG. 8

Filament cross sections showing  
distribution of microvoids

Although the majority of experiments have been performed on sapphire, several other materials including  $\text{MgAl}_2\text{O}_4$ ,  $\text{NaCl}$ , Cu-Au alloys, and  $\text{LiNbO}_3$  (3) have been grown. In general, the process is applicable to any material for which a nonreactive die material which is wet by the liquid can be found. An essentially infinite variety of cross-sectional shapes may be grown, in some cases of a complexity impossible to fabricate by conventional methods.

#### Acknowledgments

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