Oct. 7, 1969 H. E. LA BELLE, JR 3,471,266

GROWTH OF INORGANIC FILAMENTS

Filed May 29, 1967 2 Sheets-Sheet 1

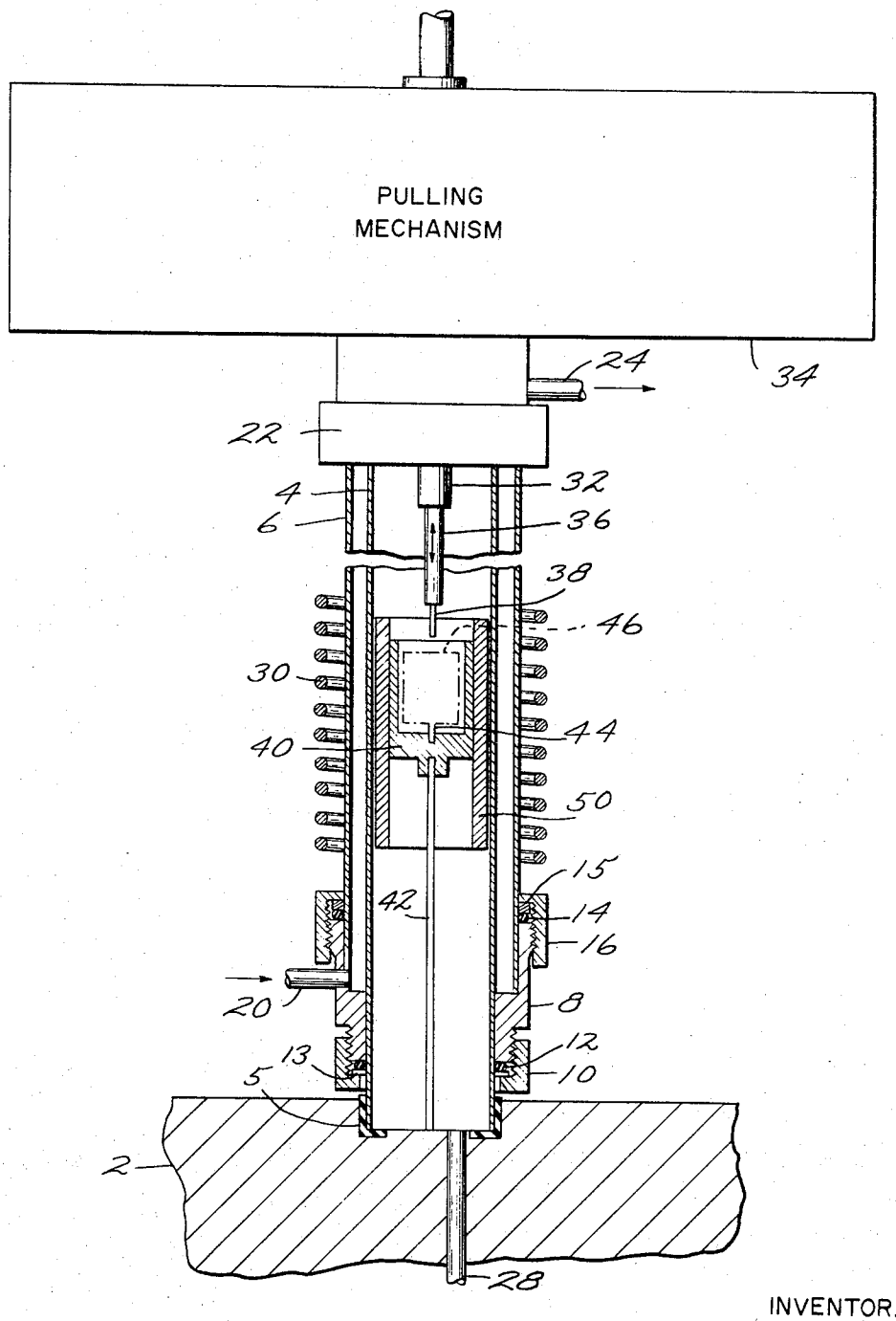

FIG. 1

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Filed May 29, 1967 2 Sheets-Sheet 2

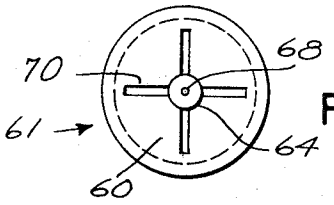


FIG. 2A

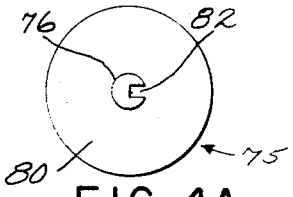


FIG. 4A

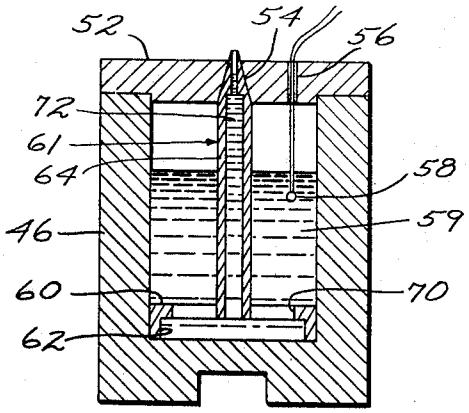


FIG. 2

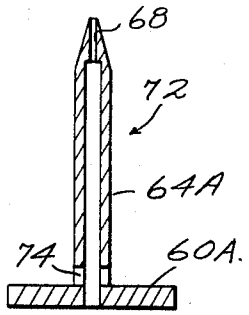


FIG. 3

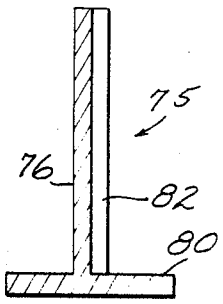
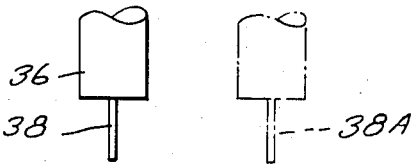


FIG. 4



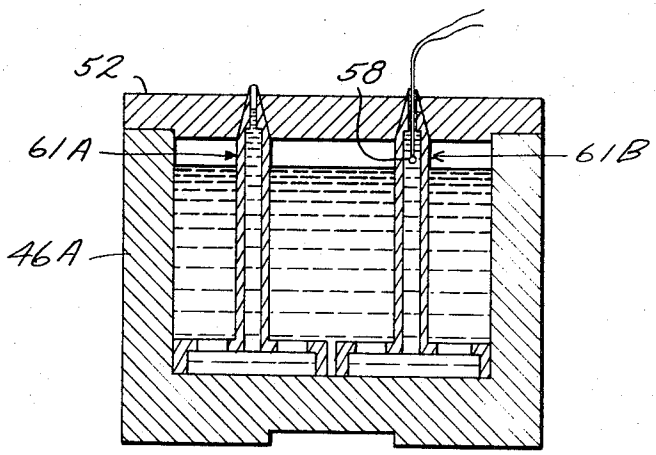


FIG. 5

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GROWTH OF INORGANIC FILAMENTS

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Continuation-in-part of application Ser. No. 582,420, Sept. 27, 1966. This application May 29, 1967, Ser. No. 641,837

Int. Cl. B01j *17/20;* C01f *7/02, 9/00*

U.S. Cl. 23—301 18 Claims

ABSTRACT OF THE DISCLOSURE

A method of growing from the melt extended filaments of α-alumina and other inorganic materials. The method involves producing a liquid column of the melt material by capillary action, introducing a seed crystal into a selected region of the column in which the thermal distribution is conducive to crystal growth propagating axially in the column, and withdrawing the seed crystal at a speed corresponding to the rate of crystal growth. Several filaments may be grown simultaneously.

This application is a continuation-in-part of my prior copending application Ser. No. 582,420, filed Sept. 27, 1966, for "Growth of Sapphire Filaments."

This invention is related to the invention disclosed and claimed in the following co-pending applications of Abraham I. Mlavsky and Harold E. La Belle, Jr.: Ser. No. 621,731, filed Feb. 14, 1967, for "Method and Apparatus for Growing Inorganic Filaments"; and Ser. No. 666,304, filed Sept. 8, 1967, for "Method and Apparatus for Growing Inorganic Filaments, Ribbon From the Melt."

This invention relates to growth from the melt of extended filaments of inorganic refractory materials.

It is recognized that a number of well known materials exhibit a marked improvement in certain of their mechanical properties, notably a great increase in tensile strength, when produced in the form of small single crystal fibers (also called "whiskers"). It is further recognized that strong composite structural materials can be made by inclusion of such fibers in selected metal or plastic matrices. Depending upon the composition of the reinforcing fibers and the matrix in which the fibers are dispersed, such composite materials have utility in the fabrication of a variety of structural members, e.g., parts for vehicles, motors, electrical devices, etc. Among the materials that offer substantial potential with respect to reinforcing metal matrices to provide high temperature structural components are beryllium, boron, and refractory oxides such as BeO, MgO, Zr_2O_3, and α-Al_2O_3. However, in the form of small crystal fibers their utility is limited—they are difficult to handle and the task of dispersing them more or less uniformly in a matrix material is formidable and time consuming at the present state of the art.

In my copending application Ser. No. 582,420, I have disclosed a method by which alumina and other high melting point inorganic materials can be grown from the melt as indefinitely long filaments with favorable mechanical properties. While such filaments do not have quite the tensile strength of small whiskers, they offer the advantage of being easier to handle because of their larger diameters and indefinite lengths. Furthermore production of extended filaments offers the promise of lower manufacturing costs.

The present invention constitutes an improvement over the methods disclosed in my copending application Ser. No. 582,420 but utilizes the same concept of growing filaments from a melt under conditions conducive to growth

propagated vertically in the melt. My earlier method utilizes a radiation shield that floats on the surface of the melt and has an orifice through which a seed crystal is inserted into and withdrawn from the melt. The seed crystal is held in the melt just long enough for crystal growth to occur thereon and is withdrawn at a rate not exceeding the rate of crystal growth in an axial direction so that successive accretions of grown crystal form an extended filament of indefinite length.

My prior method operates well but suffers from several limitations. The radiation shield must float evenly on the melt's surface. Occasionally, however, it will tilt in the crucible and will not right itself, in which case the angle between the orifice axis and the axis along which the seed is being withdrawn may be so large as to cause an interruption in the growth process. A further problem is that the radiation shield drops down in the crucible as the melt is depleted. If the height of the crucible is relatively large so that there exists a substantial temperature gradient from top to bottom, the temperature at the orifice will tend to change as the radiation shield drops lower. Accordingly periodic adjustment of the heating rate may be necessary to perpetuate in the immediate vicinity of the orifice the thermal conditions conducive to crystal growth propagated vertically. An alternative approach is to limit the vertical temperature gradient by using a relatively shallow crucible. However this latter approach is objectionable because it limits the crucible's capacity.

The general object of this invention is to provide an improved method and apparatus by which selected high melting point inorganic crystalline materials can be grown as indefinitely long filaments having improved mechanical properties.

A further object of the invention is to provide an improved method and apparatus for growing one or more extended filaments of selected high melting point materials from the melt by a growth process which appears to be dendritic, i.e., below the surface and in a supercooled region of the melt.

A more specific object is to provide a method and apparatus whereby filaments of materials such as sapphire (alpha alumina), beryllium oxide, chromium oxide and magnesium oxide can be grown from the melt at relatively high rates.

The foregoing and other objects are attained by providing a melt of a selected high melting point material that melts congruently (i.e., a material whose composition remains the same as it is converted from the solid to the liquid state and vice versa), producing a liquid column of said material from said melt by capillary action, controlling the heating of the melt so as to establish at a selected zone in said column a thermal distribution that is conducive to crystal growth propagated vertically, introducing a seed crystal into the said zone for a period sufficient for vertical growth to be initiated, and then withdrawing the seed at a rate not exceeding the rate at which the vertical crystal growth occurs in said column. The column is established within a passageway defined by mechanical means disposed in the crucible and means including a radiation shield are provided for maintaining the necessary thermal distribution in the melt without interfering with withdrawing of the seed and the extended filament grown thereon. Several filaments may be grown simultaneously by establishing a plurality of liquid columns and using a plurality of seed crystals.

Other objects and many of the attendant advantages of the present invention are believed to be apparent from the following detailed description which is to be considered together with the accompanying drawings, wherein:

FIG. 1 is an elevational section view, partly in schematic form, of one form of furnace employed in growing

crystalline filaments according to the present invention;

FIG. 2 is a longitudinal sectional view of means for forming a liquid column of melt by capillary action;

FIG. 2A is a plan view of part of the apparatus shown in FIG. 2;

FIG. 3 is a longitudinal sectional view of a modified form of means in which the liquid column is formed;

FIG. 4 is a view similar to FIG. 3 of another embodiment of the means in which the column of liquid is formed;

FIG. 4A is a plan view of the embodiment shown in FIG. 4; and

FIG. 5 is a view similar to that of FIG. 2 but relating to a different embodiment of the invention.

The following description of the invention is directed to growth of sapphire (α-alumina) filaments, but it is to be appreciated that the invention is applicable to the growth of other refractory materials that melt congruently.

In connection with my prior method, it has been determined that with respect to an open melt, α-alumina tends to grow circumferentially, i.e., radially from a seed introduced into the melt, rather than propagating down into the melt, so that any dendritic growth that occurs is generally parallel to the surface of the melt and tends to be characterized by branching of the dendrites. Variations in pulling speed do not change the direction of crystal propagation. It has been determined also that the temperature distribution about and within the region of crystal growth is a critical parameter affecting the direction of growth and that crystal growth can be made to propagate vertically in the melt in a manner permitting the pulling of a continuous filament if proper temperature distribution is achieved. More specifically, if the average temperature of the melt is maintained at a level slightly above its melting point and if the melt surface is properly shielded against radiative heat loss, it is possible to achieve in and about the region selected for crystal growth a thermal distribution that is conducive to vertical rather than horizontal propagation of the growing crystal. The means used to prevent radiative heat loss from the melt's upper surface should be so disposed that its coaction with respect to the growth region will not vary substantially as the melt is depleted; otherwise the thermal distribution within the melt may be upset and the growth may shift from vertical to horizontal propagation. It also is essential that the radiation shield not interfere with withdrawal of the continuously growing filament. Although the precautions required to be taken to successfully grow extended filaments of α-alumina are substantially as outlined above, the exact mechanism of growth is not known with certainty. However, the available evidence (such as the tendency for growth of dendrites along the melt's surface under improper thermal conditions and the rapid rate of filament growth) indicates that the growth process is dendritic, occurring below the surface in a super-cooled region of the melt. The heat shield helps establish the correct temperature distribution required to promote crystal propagation vertically and also facilitates super-cooling in the region where the seed is introduced. Adjustment of the rate of heating also helps provide the correct degree of supercooling about and adjacent to the regions of dendritic crystal growth on the inserted seed crystal. It should be noted that alumina can be supercooled substantially and I have been able to supercool molten alumina in a molybdenum crucible in excess of 100° C. measured with a W—25% Rh, W—3% Rh thermocouple.

Inherent in my prior method and also the present invention is the concept of growth filaments from a small diameter body of melt which is continuously replenished from a larger body of melt. With respect to my prior method which may be described as the "floating orifice technique," filament growth occurs in the orifice of the floating radiation shield. This orifice may be likened to a relatively small diameter secondary "crucible" filled with melt material which is continuously replenished from the larger body of melt which is contained in a relatively large diameter primary crucible (the radiation shield floats on the surface of the larger melt body). With respect to the present invention the small diameter secondary "crucible" takes the form of a hollow tube or a rod with a longitudinal slit that is positioned within and projects up out of a large melt-containing primary crucible. Capillary action causes melt material to rise within and fill the hollow tube (or the slit in the rod). The height to which the column of molten alumina will rise is an inverse function of the tube diameter. The surface energy of molten alumina being known (690 ergs./cm.^{2}), the distance a molten alumina column can rise in a given tube above the surface of the large melt body due to capillary action can be approximated from the equation

$$h=2T/drg$$

where h=the distance in cm. that the column will rise, T=the surface tension in dynes/cm., d=the density of molten alumina in gms./cc., r=the internal radius of the tube in cm., and g=the gravitational constant in cm./sec.^{2}. Thus, by way of example, for a tube of 0.75 mm. internal diameter the column would be expected to rise more than 11 cm. Hence relatively long columns can be achieved by capillary action.

Referring now to FIG. 1, the illustrated apparatus provided in accordance with the present invention comprises a vertically movable horizontal bed **2** on which is supported a furnace enclosure consisting of two concentric-spaced quartz tubes **4** and **6**. At its bottom end the inner tube **4** is positioned in an L-gasket **5** in the bed. Surrounding tube **4** is a sleeve **8** that screws into a collar **10**. Between sleeve **8** and collar **10** is an O-ring **12** and a spacer **13**. The O-ring **12** is compressed against tube **4** to form a seal. The upper end of sleeve **8** is spaced from tube **4** so as to accommodate the bottom end of tube **6**. The bottom end of tube **6** is secured in place by an O-ring **14** and a spacer **15** compressed between a collar **16** that screws onto sleeve **8**. Sleeve **8** is provided with an inlet port fitted with a flexible pipe **20**. The upper ends of tubes **4** and **6** are secured in a head **22** so that they remain stationary when the bed is lowered. Head **22** has an outlet port with a flexible pipe **24**. Although not shown, it is to be understood that head **22** includes means similar to sleeve **8**, O-rings **12** and **14**, and collars **10** and **16** for holding the two tubes in concentric sealed relation. Pipes **20** and **24** are connected to a pump (not shown) that continuously circulates cooling water through the space between the two quartz tubes. The interior of the furnace enclosure is connected by a pipe **28** to a vacuum pump or to a regulated source of inert gas such as argon or helium. The furnace enclosure also is surrounded by an R.F. heating coil **30** that is coupled to a controllable 500 kc. power supply (not shown) of conventional construction. The heating coil may be moved up or down along the length of the furnace enclosure and means (not shown) are provided for supporting the coil in any selected elevation. At this point it is to be noted that the circulating water not only keeps the inner quartz tube at a safe temperature but also absorbs most of the infrared energy and thereby makes visual observation of crystal growth more comfortable to the observer.

The head **22** is adapted to provide entry into the furnace enclosure of an elongate pulling rod **32** that is connected to and forms part of a conventional crystal pulling mechanism represented schematically at **34**. It is to be noted that type of crystal-pulling mechanism is not critical to the invention and that the construtcion thereof may be varied substantially. Preferably, however, I prefer to employ a crystal pulling mechanism that is hydraulically controlled since it offers the advantages of being vibration-free and providing a uniform pulling speed. Regardless of its exact construction which is not required to be

described in detail, it is to be understood that the pulling mechanism **34** is adapted to move pulling rod **32** axially at a controlled rate. Pulling rod **32** is disposed coaxially with the quartz tubes **4** and **6** and its lower end has an extension in the form of a metal rod **36** that is adapted to function as a holder for a seed crystal **38**.

Located within the furnace enclosure is a cylindrical heat susceptor **40** made of carbon. The top end of susceptor **40** is open but its bottom end is closed off by an end wall. The susceptor is supported on a tungsten rod **42** that is mounted in bed **2**. Supported within susceptor **40** on a short tungsten rod **44** is a crucible (shown in phanton at **46**) adapted to contain a suitable supply of alumina. The crucible is made of a material that will withstand the operating temperatures and will not react with or dissolve in the molten alumina. In the illustrated embodiment the crucible is made of molybdenum, but it also may be made of iridium or some other material with similar properties with respect to molten alumina. The molybdenum crucible must be spaced from the susceptor since there is a eutectic reaction between carbon and molybdenum at about 2200° C. The inside of the crucible is of constant diameter and may have a hemi-spherical bottom. In order to obtain the high operating temperatures necessary for the process, a cylindrical radiation shield **50** made of carbon cloth is wrapped around the carbon susceptor. The carbon cloth does not appear to couple directly to the RF field but greatly reduces the heat loss from the carbon susceptor. At a given R.F. power setting the shield **50** increase the susceptor temperature by as much as 500° C.

Referring now to FIG. 2 the crucible **46** supported within the susceptor **40** is provided with a molybdenum heat shield in the form of a cover **52**. This heat shield has a centrally located opening **54** and a second smaller opening **56** to one side of opening **54**. A thermocouple **58** is disposed in the crucible below the surface of the melt **59** formed therein, the lead wires of the thermocouple passing through the opening **56** and being connected to a responsive temperature indicating unit (not shown) of conventional design. The opening **54** is tapered conically as shown.

Situated in the crucible is a member **61** comprising an annular plate **60** formed with a depending skirt **62**. The skirt **62** maintains the plate **60** elevated above the bottom of the crucible. Formed integral with the plate **60** is an elongate tube **64** which, in the embodiment illustrated, projects up beyond the upper end of the crucible. The upper end of tube **64** is tapered so as to fit in the opening **54** and also so that its end edge is narrow. The tube **64** is open at both ends and has a substantially constant diameter from its bottom and up to and just short of its upper end, with the remaining portion having a reduced inside diameter to form a growth orifice **68**. Plate **60** is provided with a number of openings **70** spaced around the tube **64**. In a typical embodiment of the invention using a crucible **46** with an I.D. of about 0.625 inch, the tube **64** had an inside diameter of 1/16 inch except for its top end which had a growth orifice of about 0.010 inch diameter and about 1/8 inch long; the tube also had an overall length of about 4/8 inch. The plate **60** was silghtly smaller than 0.625 inch and its skirt had a height of about 1/8 inch. However, these dimension are not critical and the internal diameter of the tube, as well as its length, may be varied over a relatively wide range and still provide satisfactory results. The important thing is that the internal diameter of the tube be such that a column of molten alumina will rise therein up to its top end substantially as shown at **72** in FIG. 2. Further by way of example but not limitation, growth of alumina filaments has been achieved in tubes having a growth orifice in the range of about 0.003 to about 0.025 inch. The tube length preferably is within the range of 1/2 to 3 inches. The inside diameter of the tube below the growth orifice may vary substantially and is limited only to the extent that it provides the necessary capillary action. Hence the inner diameter of the tube could be the same as that of the growth orifice throughout its length, but this is not necessary for satisfactory operation. In the course of practice of this invention, filament growth occurs in or just below the growth orifice. As a consequence of growth and withdrawal of the filament the column of molten alumina tends to be depleted; however, the solid-liquid interface remains at the same level due to continued replenishment of the column by inflow of molten material from crucible **46** via holes **70**. Continued growth of filaments will cause the level of the melt in crucible **46** to drop, but the column will continue to exist until no further reservoir of melt exists in crucible **46**.

FIG. 3 shows a different form of member **72** that may be used to promote the rise of a column of molten alumina in crucible **46**. In this case a tube **64A** forms an extension of an annular plate **60A** which rests on the floor of the crucible. Tube **64A** is identical to tube **64** shown in FIG. 2 except that it has one or more radial ports **74** at its botom end. When this device is placed in crucible **46**, the melt will pass through ports **74** and then rise in the tube to a level above that of the surface of the melt in the crucible by capillary action.

FIG. 4 shows still another form of member **75** for promoting the rise of a column of alumina in crucible **46**. This further modification consists of an elongate rod **76** extending upward from a flat annular plate **80**. The rod **76** is formed with a longitudinal slot **82** having a cross-sectional area such that the surface tension will cause a column of molten alumina to rise up in the slot to the top end thereof when the member **75** is disposed in a crucible in place of the corresponding member **61** shown in FIG. 2. In one model of the embodiment shown in FIG. 4 the rod had a diameter of 3 mm. and a longitudinal slit along its axis measuring 0.05 centimeter x 0.2 centimeter in cross-section and about 1.0 centimeter long. The latter dimension depends, of course, on the height of the crucible in which the member is situated. The advantage of using the embodiment of FIG. 4 is that with the cover removed it permits continuous direct observation of the column of molten material, whereas only the top of the meniscus of the melt column can be seen in tubes **64** and **64A**. With all three embodiments the radiation shield, i.e., the cover **52**, and the top end of the liquid column in which crystal growth occurs remain in substantially constant relation to each other as the melt in crucible **46** is consumed. More specifically, the top end of the column is constantly surrounded by the radiation shield.

FIG. 5 illustrates still another embodiment of the invention. In this case a crucible **46A** is employed that has an internal diameter large enough to accept two of the members **61** (or members **72** or **75**). One member **61A** is used for filament growth on seed **38**. The other member **61B** provides a melt column whose temperature is monitored by thermocouple **58**. Since the arrangement of the two tubes **64** is radially symmetrical, the melt columns therein will exhibit substantially the same thermal distribution. Hence by positioning thermocouple **58** in member **61B** it is possible to achieve an approximate indication of the temperature in the region of the melt column in member **61A** where filament growth is occurring. The indication provided by thermocouple **58** is helpful in understanding the growth process occurring simultaneously in member **61A** and in programming the controls for the heating element **30** so as to properly adjust the thermal conditions of the melt. Of course, by removing thermocouple **58** and inserting a seed crystal **38A** into tube **61B**, it is possible to grow two filaments simultaneously. It is further contemplated that crucible **46A** could be made large enough to accommodate more than two members **61**, e.g. six of them, in a symmetrical array so that more than two filaments could be pulled at the same time. In such multiple filament growth the

different seed crystals may be attached to a common pulling mechanism or to separate pulling mechanisms, and one of the members **61** may be reserved for a thermocouple positioned in the manner shown in FIG. 5. It is to be noted that multiple filament growth also is possible with the "floating orifice technique," but with far less reliability and far more difficulty than is the case with this further invention.

Operation of the apparatus of FIG. 1 using the crucible arrangement of FIG. 2, and an example of the method of growing alpha-alumina filaments according to my invention will now be described. An α-alumina seed crystal **38** is mounted in holder **36** with its C-axis aligned parallel to the holder's path of movement. At the same time a quantity of substantially pure α-alumina is placed in crucible **46**, cover plate **52** is set in place, and then crucible **46** is placed within susceptor **40** on tungsten rod **44**. Access to the seed holder and the susceptor is achieved by lowering bed **2** away from the furnace enclosure and lowering the seed holder to below the bottom end of tube **4**. With the bed restored to the position of FIG. 1, cooling water is introduced between the walls of the two quartz tubes, and the enclosure is evacuated and then filled with helium. The latter is kept at a pressure of about 1 atmosphere thereafter. Then the R.F. coil is energized and operated so that the α-alumina is brought to a molten condition. The α-alumina is brought to a temperature slightly above its melting point which is in the range of 2040 to 2050°. In this molten condition the alumina will rise in the capillary tube **64** so that its meniscus is substantially flush with the top end of the tube. Once temperature equilibrium is established, the pulling mechanism is actuated and operated so as to bring the seed crystal **38** into the growth orifice **68** to a depth of about 0.5 mm. below the meniscus of the melt column. It is allowed to rest there for about five seconds. Thereafter the pulling mechanism is operated so as to withdraw the seed crystal at a rate of about 150 mm./min. It should be noted that the parameters of depth, rest time of the seed in the melt column, and the pulling rate are related and are determined by trial and error for the particular apparatus employed and the temperature of the melt column surrounding the seed. The melt temperature is critical and in the usual case initial withdrawal of the seed is unaccompanied by continuous growth. At this point it is to be appreciated that if the upper end of the melt column is too cold, nothing will happen when the seed touches the meniscus; on the other hand, if the upper end of the melt column is too hot, the seed will melt. The temperature of the melt is adjusted accordingly and the seed again is brought into contact with the melt. Attainment of the proper melt temperature is indicated by commencement of dendritic growth on the end of the seed. Thereafter the seed is withdrawn at a speed corresponding to the rate at which the dendrite growth propagates down into the melt. However, the operator may have to vary the melt temperature and the pulling rate to some degree to optimize the growth process. If the seed continues to be withdrawn at the proper speed the growth will be continuous until the melt is depleted. The maximum filament length has been limited only by the maximum pulling distance afforded by pulling mechanism **34**. The diameter of the grown filament may be varied by adjusting the pull rate and/or the temperature of the melt column.

By using a thermocouple positioned in the manner shown in FIG. 5 so that it sees a thermal environment similar to that surrounding the seed **38** when positioned in the growth orifice, I have been able to determine that the temperature in the growth region need not be held constant in order to achieve continuous filament growth. Instead the temperature may vary over a narrow range with the extent of the range depending upon the pulling speed. The operative temperature range narrows with higher pulling speeds and widens with lower pulling speeds.

The habit of the filament-like crystals produced according to the foregoing method has shown variations that can be generalized into four different types, all of which have been grown using a sapphire seed crystal oriented with the C-axis parallel to the axis of the seed holder. One habit is characterized by a rather uniform outer surface and a circular cross-section. The other habits all have more or less rectangular cross-sections, but the outer surface of one has irregular undulations, another is stepped longitudinally, and the third appears to be twisted longitudinally. All of these different habits have easily discernible features. After a particular habit has been nucleated and propagated, it is possible to separate the grown filament from the melt by fast retraction, reinsert it into the melt, and then resume normal growth procedure. The dendrite filament that grows afterward will be the same type as that orginially propagated before separation from the melt.

Laue X-ray back reflection photographs of α-alumina filaments made according to the foregoing procedure reveal certain interesting facts, notably that the filaments are comprised of one or two and in some cases, three or four crystals growing together longitudinally separated by a low angle (within 3° of the C-direction) grain boundary. Thus one Laue photograph of a filament grown on a C-axis oriented sapphire seed revealed three-fold symmetry except that each reflection was split into three or four spots, suggesting the presence of three or four crystals with their C-axes approximately parallel to the filament axis but slightly misoriented with respect to each other. Other filaments give still more complex patterns but generally still with the features of three-fold symmetry. Those filaments that appear to be twisted longitudinally may in fact be twinned since the crystal ends often are characterized by two discrete points. However, the essential aspect of this invention is that the seed crystal should be mounted so that growth occurs along its C-axis <0001>, i.e., with its C-axis extending along or parallel to the axis of movement of the crystal holder. While growth will occur on a seed mounted so that its C-axis is at an angle to the seed holder, an inferior product results. Filaments growing in the C-direction have smoother surfaces and have superior strength while filaments growing off of the C-direction, e.g. by as much as 10° have irregular surfaces and are weaker.

For convenience and in the interest of avoiding any suggestion that the filaments are polycrystalline in character, I prefer to describe my filaments as "monocrystalline," it being understood this term is intended to embrace a filament of indefinite length which over any given portion of its length exceeding its maximum cross-sectional dimensions is comprised of a single crystal or two or more single crystals growing together longitudinally but separated by a relatively small angle (i.e. less than 4°) grain boundary.

A further interesting phenomenon is that the cross-sectional shape and sizes of the filaments do not conform to the shape and size of the orifice through which they are pulled. This is different from what occurs in other crystal growing processes where a melt is extruded through a die. Thus, for example, in the process disclosed in U.S. Patent No. 3,124,489, issued Mar. 10, 1964, to F. F. Vogel, Jr. et al. for "Method of Continuously Growing Thin Strip Crystals," the germanium ribbon pulled from the melt through a carbon die has a cross-section of the same shape and substantially the same area as the die passage exit. The difference is attributable to the fact that in my process the crystal grows dendritically down into the melt, i.e., the solid/liquid interface of the filament is below the melt surface, while in the process of Vogel et al. the molten material solidifies within or above the die passage. The tubes and slit rods used in my process do not shape the filament, except insofar as

they shape the temperature gradients. The filament shape appears to be effected by the temperature gradients, the average temperature of the melt, and the orientation of the seed crystal. The rate of pull affects the size of the filament and also appears to some extent to affect its shape. It also is to be noted that the process need not be carried out in a helium or argon atmosphere, but instead the furnace enclosure may be evacuated to a suitable level.

While a molybdenum cover plate is not essential, its use does improve the thermal distribution of the melt both in the crucible and in the capillary tube. In this connection it appears that molybdenum has a lower total emissivity than alumina at temperatures in the order of 2000° C. It is believed that this property is responsible for its apparent ability to limit the heat loss from the melt and control the radial and longitudinal temperature gradients in the larger melt body as well as in the capillary tube. This heat shielding effect not only helps establish the correct temperature distribution required to promote crystal propagation vertically but also permits the column to be supercooled in the region where the seed is introduced. Of course the tube itself functions as a heat shield as well as providing an exposed central growth orifice of any chosen diameter.

A definite indication of the fact that growth is dendritic is the speed at which the filament may be pulled from the melt, e.g. up to about 150 mm./min., using a tube with an orifice having a diameter of about 0.0250 inch. This is substantially in excess of the one inch/min. speed employed in growing germanium strip crystal using the process of Vogel et al., cited above. It is believed that growth rates substantially faster than 150 mm./min. can be achieved if the heat loss from the filament (primarily radiative in the apparatus and process described above) is augmented by forced convection.

In addition to the fact that it permits growth of alumina in filament form, the invention has several other advantages. For one thing the apparatus for producing thermal conditions essential to dendritic growth is simple and the capillary tube is not restricted to use with the particular furnace or crucible design illustrated in the drawings but may be employed in other apparatus employed in rowing crystals from a melt. Another advantage is that the process may be used to grow ruby filaments. Perhaps the most important advantage is that it provides a new and useful form of α-alumina, i.e., extended filaments. In this connection it is to be noted that I have grown sapphire filaments measuring 12 inches in length (and 0.05 to 0.50 mm. in diameter) at pulling rates up to 150 mm./min. It is to be appreciated that the length of these filaments was not limited by the process per se but only by the capability of pulling mechanism **34**, and production of filaments with lengths in the order of tens of feet and higher is contingent only upon provisions of apparatus of greater pulling capacity. Sample sapphire filaments produced in the manner described above have been found to have an elastic modulus of at least 30×10^6 and more commonly in the range of $50\text{–}70\times10^6$ p.s.i., and a tensile strength in the range of 150,000–400,000 p.s.i. To date, those filaments exhibiting the greatest tensile strength have been characterized by a rounded triangular cross-section with a substantially three-fold symmetry about the C-axis so that the edges of the triangle correspond to major planes in the crystal.

A further advantage of the invention is that it is applicable to growth of filaments of other materials that melt congruently and have a hexagonal crystal structure like α-alumina, notably BeO, Cr_2O_3. It also may be applicable to growth of certain materials with cubic structure, such as MgO. The process for growing these materials differs from the process of growing sapphire filaments in that it requires different operating temperatures because of different melting points. Additionally certain minor changes are required in the apparatus, e.g., different crucible materials in order to avoid reaction between the melt and the crucible.

As used herein the term "filament" is not limited to a crystalline product of circular cross-section but also embraces other cross-sectional geometries, including polygonal. However, it is a characteristic of this invention that for a particular filament, the cross-section will not continually vary over its length.

It is to be understood that the invention is not limited in its application to the details of apparatus and method specifically described or illustrated, and that within the scope of the appended claims, it may be practiced otherwise than as specifically described or illustrated.

I claim:

1. Method of growing a continuous monocrystalline filament of a crystalline material from a reservoir body of a melt thereof using a member having a capillary communicating with said reservoir body, including establishing in said capillary principally by action of capillary rise a column of said melt that projects up out of said reservoir body, adjusting the temperature of said column of melt so as to provide therein at the upper end of said capillary a zone conducive to crystal growth of said material propagating vertically in said column, inserting a seed into said zone so that crystal growth of said material can commence thereon, and withdrawing said seed at a rate not exceeding the rate at which said crystal growth occurs so that successive crystalline accretions of said material form a continuous filament.

2. Method of claim **1** wherein said material melts congruently.

3. Method of claim **1** wherein said material is a member of the group consisting of beryllium oxide, magnesium oxide, chromium oxide and aluminum oxide.

4. Method of claim **1** wherein said material is α-alumina.

5. Method of claim **1** wherein said reservoir body and said column of melt are maintained in an inert environment.

6. Method of producing a continuous filament of a crystalline material comprising, providing a crucible including in its interior means substantially stationary with respect to the vertical disposition thereof defining a capillary that has an open top end and communicates at some point removed from said top end with the interior of said crucible, providing in said crucible a supply of said material, heating said material to form a melt and also to produce in said capillary principally by action of capillary rise a column of said melt above the level of the melt in the crucible, adjusting the heating of said melt so as to establish in the upper end of said capillary a zone in which single crystal growth of said material will occur onto a seed inserted in said zone, inserting a seed into said zone for a period sufficient for commencement of crystal growth thereon, and pulling said seed away from said capillary at a speed corresponding to the rate at which crystal growth occurs thereon so that successive accretions of grown crystal form an extended filament.

7. Method of producing a continuous filament of a crystalline material comprising, providing a crucible including in its interior means defining a capillary that has an open top end and communicates at some point removed from said top end with the interior of said crucible, providing in said crucible a supply of said material, heating said material to form a melt and also to produce in said capillary principally by action of capillary rise a column of said melt above the level of the melt in the crucible, adjusting the heating of said melt so as to establish in the upper end of said capillary a zone in which single crystal growth of said material will occur onto a seed inserted in said zone, inserting a seed into said zone for a period sufficient for commencement of crystal growth thereon, and pulling said seed away from said capillary at a speed corresponding to the rate at which crystal growth occurs thereon so that successive accretions of grown crystal form an extended filament.

8. Method of producing a filament of a crystalline material that melts congruently comprising, providing in a crucible a mass of said material, converting said mass to a melt, establishing principally by action of capillary rise in a plurality of capillaries disposed substantially stationary in said crucible a plurality of columns of said melt each extending above the surface of said melt in said crucible, adjusting the temperature of said melt so as to establish in the upper end of each capillary a zone with a temperature conducive to crystallization of said material onto a seed, inserting a seed into each of said zones for a period sufficient for crystal growth to occur thereon, and pulling said seeds away from said capillaries at a rate not exceeding the rate at which said growth occurs so that by successive accretions of grown crystal an extended filament is formed on each seed.

9. Method of claim 7 wherein said material is alumina and said seed is a single crystal of alumina oriented so that growth of said filament is along the C-axis of said crystal.

10. Method of claim 7 wherein said crucible and said capillary-defining means are made of molybdenum and said material is alumina.

11. Method of claim 7 wherein said material is alumina and said crucible and capillary-defining means are made of iridium.

12. Method of growing a continuous filament of a selected crystalline material from a reservoir body of melt thereof using a tube with a capillary having an open end that is outside of said reservoir body and which communicates with said reservoir body by way of an opening remote from said open end that is submerged in said reservoir body, comprising filling said capillary with said melt principally by action of capillary rise from said reservoir body; establishing in the melt in said capillary at said open end a thermal zone having a temperature at which said material will crystallize on a seed, and positioning a seed so that crystallization of said material will occur thereon in said zone; pulling said seed away from said capillary at a rate consistent with the rate of crystallization of said material so that a continuous filament of said material is formed by progressive crystallization, and maintaining said capillary filled with said melt principally by action of capillary rise from said reservoir body.

13. Method of producing a filament of a crystalline material that melts congruently comprising, providing in a crucible a mass of said material, converting said mass to a melt, establishing principally by action of capillary rise in a plurality of capillaries disposed in said crucible a plurality of columns of said melt each extending above the surface of said melt in said crucible, adjusting the temperature of said melt so as to establish in the upper end of each capillary a zone with a temperature conducive to crystallization of said material onto a seed, inserting a seed into each of said zones for a period sufficient for crystal growth to occur thereon, and pulling said seeds away from said capillaries at a rate not exceeding the rate at which said growth occurs so that by successive accretions of grown crystal an extended filament is formed on each seed.

14. Method of claim 8 wherein said material is α-alumina.

15. Method of growing a continuous filament of a crystalline material from a melt thereof comprising, providing a crucible containing a melt of said material and a member substantially stationary with respect to the vertical disposition thereof having a capillary that communicates with and extends above the level of said melt and is adapted to be wet by said melt, establishing principally by action of capillary rise in said capillary a column of said melt which extends above the level of the melt in said crucible, adjusting the temperature of said column of melt so as to provide in the upper end of said capillary a zone with a temperature conducive to crystal growth of said material on a seed positioned in said zone and positioning a seed in said zone for a period of time sufficient for crystal growth to commence thereon, and withdrawing said seed away from said capillary along a predetermined axis at a rate consistent with the rate of crystal growth propagated parallel to said axis so that successive crystalline accretions of said material form a continuous filament.

16. Method of growing a continuous filament of a crystalline material from a melt thereof comprising, providing a crucible containing a melt of said material and a member with a capillary that communicates with and extends above the level of said melt and is adapted to be wet by said melt, establishing principally by action of capillary rise in said capillary a column of said melt which extends above the level of the melt in said crucible, adjusting the temperature of said column of melt so as to provide in the upper end of said capillary a zone with a temperature conducive to crystal growth of said material on a seed positioned in said zone and positioning a seed in said zone for a period of time sufficient for crystal growth to commence thereon, and withdrawing said seed away from said capillary along a predetermined axis at a rate consistent with the rate of crystal growth propagated parallel to said axis so that successive crystalline accretions of said material from a continuous filament.

17. Method of claim 16 wherein said column is maintained at a substantially constant height by inflow to said capillary member of additional melt from said crucible at a rate sufficient to replace the material consumed by growth and withdrawal of said filament.

18. Method of growing a continuous monocrystalline body of a crystalline material comprising the steps of forming a reservoir melt of said material, establishing principally by action of capillary rise from said reservoir body a column of said melt in a capillary which communicates with said reservoir body of melt, positioning a seed in said column and adjusting the temperature of said column so as to provide in said column at the interface with said seed a thermal zone in which crystallization of said melt will occur on said seed, pulling a continuous monocrystalline body from said column by progressive crystallization on said seed at said interface, maintaining said progressive crystallization by adjusting one or more crystal growth conditions such as rate of pull and melt temperature, and continually supplying additional melt to said column at a rate consistent with the rate at which the melt in said column is consumed by crystallization and withdrawal so as to maintain the height of said column and said interface substantially constant.

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U.S. Cl. X.R.

23—305

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,471,266 October 7, 1969

Harold E. La Belle, Jr.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, lines 40 to 57 should be canceled and the follow inserted instead:

6. Method of claim 1 wherein said material is alumina, and further wherein said seed is a single crystal of alumina which is oriented so that its c-axis extends in the direction of growth of said filament.

Column 11, lines 1 to 16 should be canceled and the following inserted instead:

8. Method of claim 7 further including using a heat shield which covers the top of said crucible and surrounds the upper end of said column to help maintain the thermal distribution in said zone substantially constant as said column simultaneously undergoes (a) depletion by growth and withdrawal of said filament and (b) replenishment from said melt by capillary action.

same column 11, lines 26 to 43 should be canceled and the followi inserted instead:

12. Method of growing a continuous filament of a selected crystalline material from a reservoir body of melt thereof using a capillary having an open end that is outside of said reservoir body and an opening remote from said open end that is submerged in said reservoir body, comprising filling said capillary with said melt principally by action of capillary rise from said reservoir body; establishing in the melt in said capillary at said open end a thermal zone having a temperature at which said material will crystallize on a seed, and positioning a seed so that crystallization of said material will occur thereon in said zone; pulling said seed away from said capillary at a rate consistent with the rate of crystallization of said material so that a continuous filament of said material is formed

by progressive crystallization, and maintaining said capillary filled with said melt principally by action of capillary rise from said reservoir body.

same column 11, line 60, the claim reference numeral "8" should read -- 13 --; same column 11, lines 62 to 69, and column 12, lines 1 to 12 should be canceled and the following inserted instead:

15. Method of claim 13 wherein said material is a member of the class consisting of beryllium oxide, magnesium oxide, chromium oxide and aluminum oxide.

Signed and sealed this 27th day of October 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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