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Labelle, Jr. et al.

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[54] **GROWTH OF TUBULAR CRYSTALLINE BODIES**

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[21] Appl. No.: **158,806**

[52] **U.S. Cl.** ..... **23/301 SP**, 23/273 SP, 65/89, 117/97, 264/165, 264/174

[51] **Int. Cl.** **B01j 17/18**

[58] **Field of Search** ..... 23/301 SP, 273 SP, 23/273 V; 65/89; 264/165, 174; 117/97; 118/401

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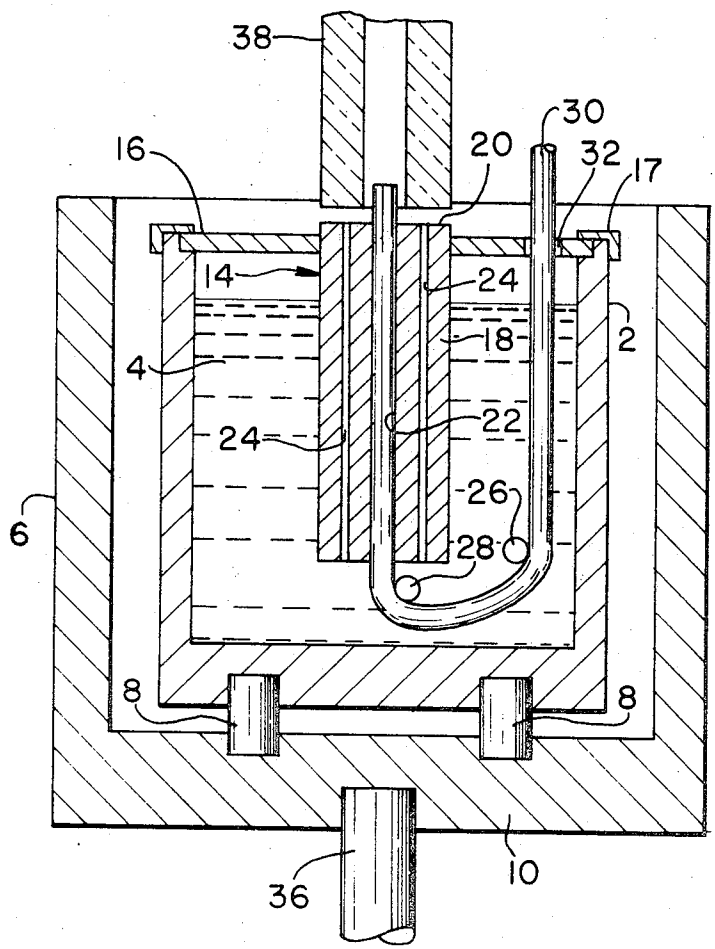
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[57] **ABSTRACT**

The invention is a method and apparatus for producing composite materials and monocrystalline capillary tubes. Monocrystalline bodies of a material such as alumina are grown from a melt about small diameter, high temperature wires or filaments so as to form high strength composites. The small wires or filaments may be removed from the composites so as to leave monocrystalline bodies with capillary size openings therein.

9 Claims, 11 Drawing Figures



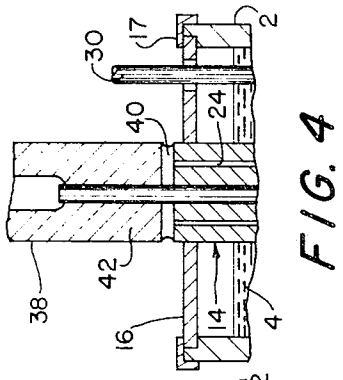


FIG. 4

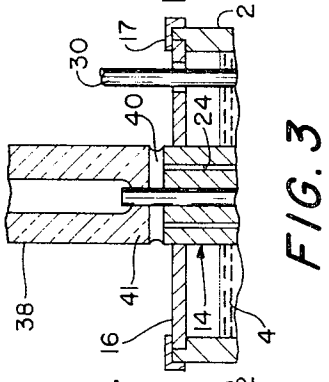


FIG. 3

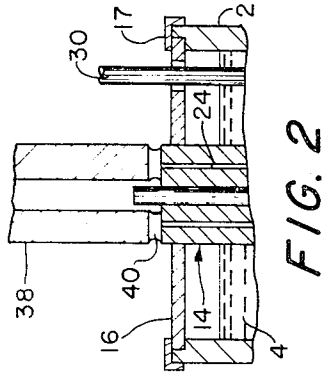


FIG. 2

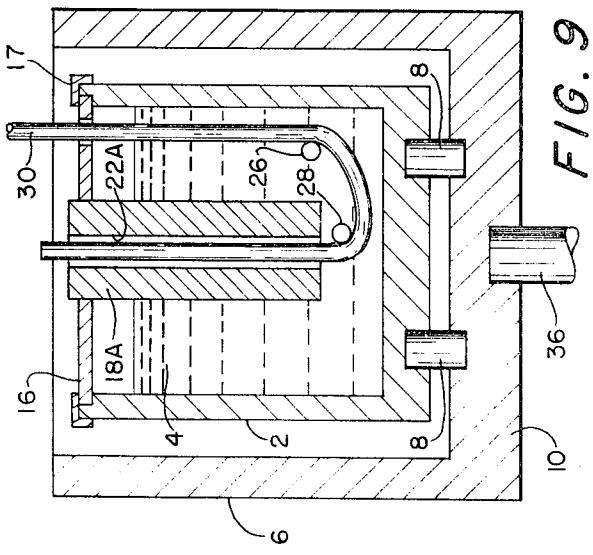


FIG. 9

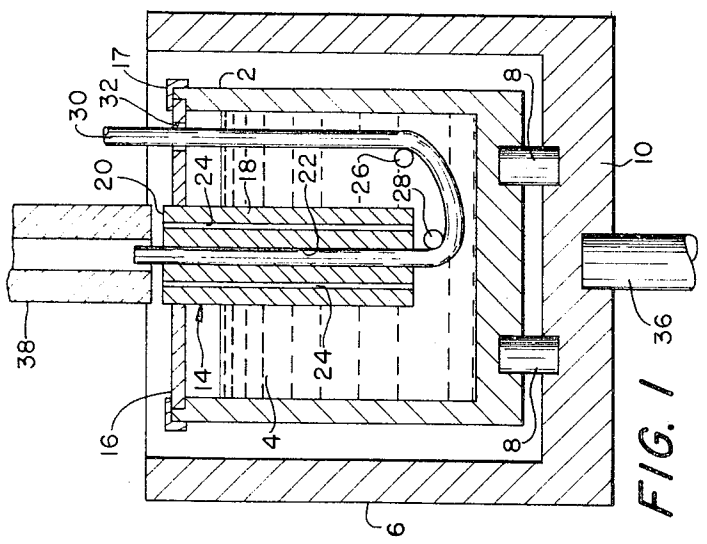


FIG. 1

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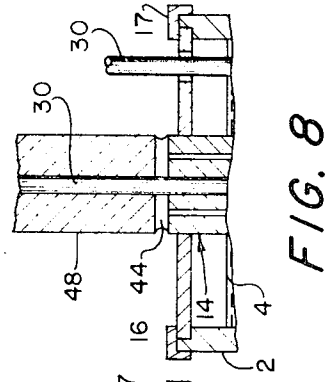


FIG. 8

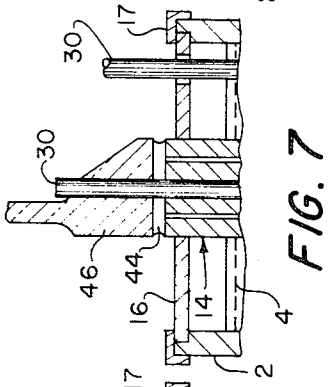


FIG. 7

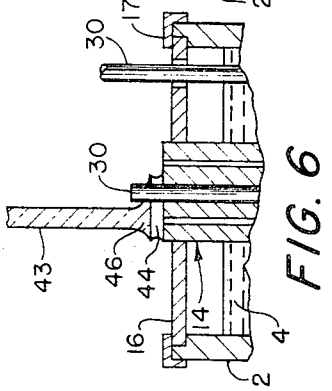


FIG. 6

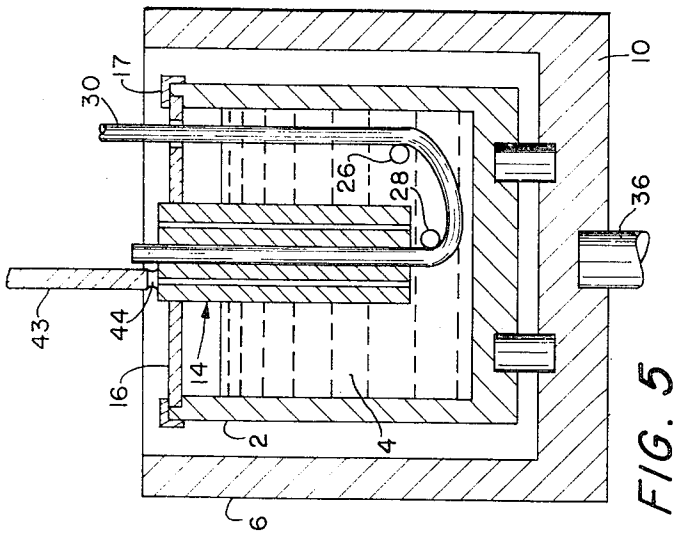


FIG. 5

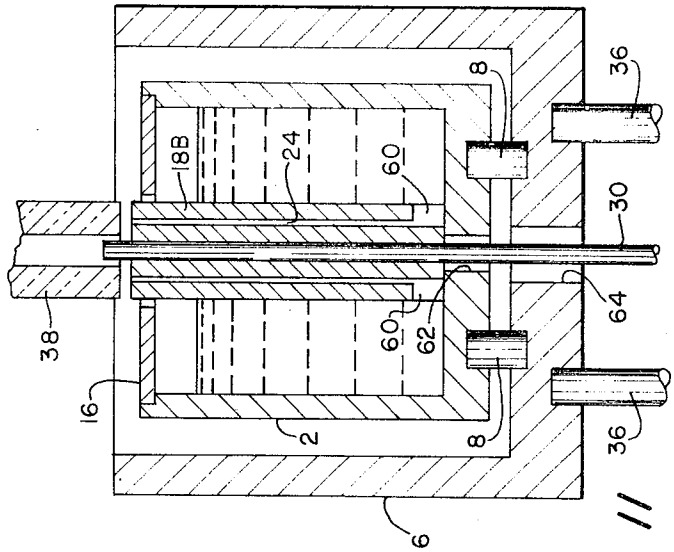


FIG. 11

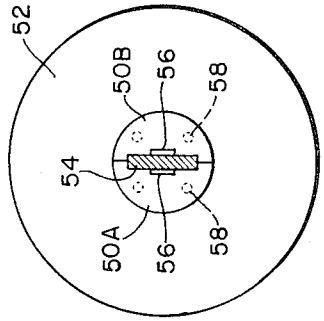


FIG. 10

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GROWTH OF TUBULAR CRYSTALLINE BODIES

This invention relates to crystal growth and more particularly to production of substantially monocrystalline bodies having wires embedded therein and substantially monocrystalline capillary tubes.

Various methods have been developed for growing monocrystalline bodies from a melt. The present invention involves growing crystalline bodies from a melt according to what is called the edge-defined, film fed, growth technique (also known as the EFG process). Details of this process are described in the copending U.S. Patent Application of Harold E. LaBelle, Jr., Ser. No. 700126, filed Jan. 24, 1968 for Method of Growing Crystalline Materials now U.S. Pat. No. 3,591,348.

In the EFG process the shape of the crystalline body is determined by the external or edge configuration of the end surface of a forming member which for want of a better name is called a die. An advantage of the process is that bodies of selected shapes such as round tubes or flat ribbons can be produced commencing with the simplest of seed crystal geometries, namely, a round small diameter seed cystal. The process involves growth on a seed from a liquid film of feed material sandwiched between the growing body and the end surface of the die, with the liquid in the film being continuously replenished from a suitable melt reservoir via one or more capillaries in the die member. By appropriately controlling the pulling speed of the growing body and the temperature of the liquid film, the film can be made to spread (under the influence of the surface tension at its periphery) across the full expanse of the end surface of the die until it reaches the perimeter or perimeters thereof formed by intersection of that surface with the side surface or surfaces of the die. The angle of intersection of the aforesaid surfaces of the die is such relative to the contact angle of the liquid film that the liquid's surface tension will prevent it from overrunning the edge or edges of the die's end surface. Preferably the angle of intersection is a right angle which is simplest to achieve and thus most practical to have. The growing body grows to the shape of the film which conforms to the edge configuration of the die's end surface. Since the liquid film has no way of discriminating between an outside edge and an inside edge of the die's end surface, a continuous hole may be grown in the crystalline body by providing in that surface a blind hole, i.e. cavity, of the same shape as the hole desired in the growing body, provided, however, that any such blind hole in the die's end surface is made large enough so that surface tension will not cause the film around the hole to fill in over the hole. From the foregoing brief description it is believed clear that the term "edge-defined, film-fed growth" denotes the essential feature of the EFG process—the shape of the growing crystalline body is defined by the edge configuration of the die and growth takes place from a film or liquid which is constantly replenished.

The primary object of this invention is to provide substantially monocrystalline capillary tubes. As used herein the term "capillary tubes" denotes an elongate body having a small diameter through bore. Capillary tubes are useful for various purposes, e.g. as thermal compression bonding tips for bonding materials such as gold wire to electronic components and integrated circuits, delivery conduits for liquids and gases in medical and analytical equipment, and fine sand blast nozzles.

Heretofore it has not been possible to produce elongate substantially monocrystalline capillary tubes of alumina or other materials, particularly other high temperature materials, in small sizes, e.g. capillaries having a diameter in the order of 0.006 inch. Relatively short, e.g. one-fourth inch long, monocrystalline capillary tubes have been possible by forming a hole in a monocrystalline boule, but no practical way exists for forming a continuous small diameter bore lengthwise in a long monocrystalline body. Attempts to grow relatively long small diameter capillary tubes by the EFG process as above-described have not been successful since the blind hole required in the die's end surface is so small that the liquid film tends to fill in over it, with the result that a solid rod rather than a tube is grown.

Accordingly a more specific object of this invention is to provide a method of growing monocrystalline capillary tubes of indefinite length according to the EFG technique.

A further object is to provide a method of growing elongate substantially monocrystalline bodies which have a wire embedded therein.

Still other objects will be obvious from the following detailed specification.

Described briefly, the invention consists of providing a die or forming member having (1) a substantially horizontal end surface that is adapted to be wet by and is used to support a film of melt from which a crystal is to be pulled, and (2) a vertical passageway or passageways through which additional melt and a wire may be fed to said surface. Melt is supplied to at least one of said passageways and rises to the top end thereof by capillary action. Then a film of melt is formed on the said end surface so as to connect with the melt in the said vertical passageway and a substantially monocrystalline body is grown from the film of melt. The film is made to fully cover the end surface of the die and the pulling speed of the growing body and the temperature of the film are controlled so that the body grows from the film along its entire horizontal expanse and around the wire. Accordingly as the growing body is pulled away from the said end surface, it draws the wire with it so that successively grown portions of the aforesaid body surround successive portions of the wire. The resulting product is a substantially monocrystalline body surrounding and gripping an elongate wire. By using small diameter wire and by removing the wire from the crystalline body after growth has been terminated, it is possible to provide substantially monocrystalline capillary tubes.

Other features and many of the attendant advantages of this invention are set forth in or rendered obvious by the following detailed description which is to be considered together with the accompanying drawings wherein:

FIG. 1 is a vertical section of one form of apparatus used in practising the invention;

FIG. 2–4 are fragmentary vertical sectional views illustrating how a monocrystalline body having a wire embedded therein maY be grown on a tubular seed using the apparatus of FIG. 1;

FIGS. 5-8 are views similar to FIGS. 1–4 showing how growth may be achieved using a seed crystal in the form of a filament;

FIG. 9 is a view similar to FIG. 2 of a modified form of apparatus for practising the invention;

FIG. 10 is a plan view of still another form of die assembly for use in growing a crystal body having a flat metal ribbon embedded therein; and

FIG. 11 is a view similar to FIG. 1 of a die assembly in which the wire is fed through an opening in the bottom of the crucible.

The present invention may be used to produce monocrystalline bodies of the character described made of any one of a variety of congruently melting materials that solidify in identifiable crystal lattices. By way of example, the material may be alumina, barium titanate, lithium niobate and yttrium aluminum garnet. The invention is also applicable to other materials, preferably those that melt congruently (i.e., compounds that melt to a liquid of the same composition at an invariant temperature). The following detailed description of the invention is directed to growing products of the character described made of sapphire, i.e., monocrystalline alpha-alumina. In the following description, like reference characters on the drawing refer to like elements in the several figures.

Turning now to FIG. 1, the illustrated apparatus comprises a crucible 2 adapted to contain a melt 4 of the material to be grown in accordance with this invention. The crucible is made of a material that will withstand the operating temperatures and will not react with or dissolve in the melt. With an alumina melt, the crucible is preferably made of molybdenum, but it may also be made of tungsten, iridium, rhenium or some other material with similar properties with respect to molten alumina. The crucible is mounted within a carbon susceptor 6 by means of a plurality of short tungsten rods 8. The top end of susceptor 6 is open but its bottom end is closed off by an end wall 10. Where a molybdenum crucible is used it must be spaced from the susceptor, as by the rods 8, since there is an eutectic reaction between carbon and molybdenum at about 2200°C.

Mounted within crucible 2 is a die assembly 14 that may be made of the same material as the crucible and which comprises a disc 16 that is locked to the crucible by a removable collar 17. In addition to functioning as a radiation shield to reduce radiative heat loss from the melt, disc 16 supports a cylindrical vertically-extending rod 18 which is securely mounted within a centrally located hole in the disc. Rod 18 extends a short distance above the disc and its bottom end terminates short of the bottom of the crucible. Rod 18 has a flat, substantially horizontal, top end surface 20, a coaxial through bore 22, and a plurality of small diameter bores 24 that are sized to function as capillaries so that the melt can rise therein by capillary action. Preferably the capillaries 24 are uniformly spaced about the axis of rod 18.

Secured to the side wall of crucible 2 and extending transversely therein are two spaced guide pins 26 and 28 located as shown. Pins 26 and 28 and the die assembly 14 are made of the same material as the crucible. Pins 26 and 28 function as guides for a molybdenum wire 30 around which the substantially monocrystalline body is to be grown. The wire 30 is sufficiently flexible to permit it to be introduced into the crucible via a suitable feed-through hole 32 in disc 16, passed under pins 26 and 28, and inserted up through bore 22. Initially the leading end of wire 30 projects at a convenient height, e.g. one-eighth inch, above the upper end surface 20 of rod 18. Wire 30 may also be made of tungsten, iridium or rhenium.

The apparatus of FIG. 1 as above-described is mounted in a suitable induction heating furnace (not shown) adapted to envelope the crucible and the growing body in an inert atmosphere, e.g. argon, and having a crystal pulling mechanism adapted to position a seed crystal and to pull the seed at a controlled rate as crystal growths occurs thereon. One form of furnace that may be used in the practice of this invention is illustrated and described in U.S. Pat. No. 3471266 issued 10/7/69 to Harold E. LaBelle, Jr. for Growth of Inorganic Filaments. The susceptor 6 is mounted within the furnace by attaching it to the upper end of a tungsten support rod 36 that is mounted in the furnace. Rod 36 may be mounted to the base 2 of the furnace shown in U.S. Pat. No. 3471266.

The height of the upper end surface 20 of rod 18 relative to the bottom of the crucible and the diameter of bores 24 are such that molten alumina can rise in and fully fill the capillaries 24 by action of capillary rise so long as the level of the melt in the crucible is high enough to trap the bottom end of rod 18.

Crystal growth may be initiated using a tubular or non-tubular seed. Thus it is possible to start with an α-alumina seed in the form of a monocrystalline filament or ribbon and grow a tube onto the seed from a film supported on end surface 20 by progressively expanding the film and crystal growth in a horizontal direction as growth occurs vertically. Preferably, however, it is preferred to use a monocrystalline tube previously grown by the EFG technique. Such tubes are available commercially.

FIGS. 1–4 illustrate how an α-alumina capillary tube may be grown according to the invention using a monocrystalline tube of alumina as the seed. Assume for ease of description that the crucible 2 and susceptor 6 are mounted in an induction furnace of the type described in U.S. Pat. No. 3471266 in which an argon atmosphere is maintained and the crucible and capillaries 24 are filled with an alumina melt. Assume also that a molybdenum wire 30 has been inserted up through the center hole 22 of rod 18 as shown and that a seed in the form of a previously grown sapphire tube 38 having an internal diameter large enough to fit over the upper end of wire 30 is supported by the crystal pulling mechanism of the furnace in coaxial alignment with rod 18. With the upper end surface 20 of rod 18 at a temperature about 10°–40°C higher than the melting point of alumina, the seed tube 38 is lowered over the projecting end of wire 30 into contact with surface 20 and held there long enough for the end of the tube to melt and form a liquid film 40 that connects with the melt in the capillaries 24 (see FIG. 2). It is to be noted that the capillaries are shown empty in FIGS. 1–4 in order to render the capillaries more distinct to the reader. It is to be understood that before the end of tube 38 is melted to form film 40, the melt in each capillary has a concave meniscus with the edge of the meniscus being substantially flush with surface 20. The temperature gradient along seed tube 38 is one factor influencing how much of the tube melts and the thickness of film 40. In this connection it is to be noted that the seed tube functions as a heat sink so that its temperature is lower at successively higher points thereon. However, the thermal gradient along tube 38 is affected by the power input to the furnace's induction heating coil and the relative dispositions of the heating coil and susceptor 6. In practice these parameters are adjusted so

that the film **40** has a thickness in the order of 0.1 mm.

Once the film **40** has connected with the melt in the capillaries, the pulling mechanism is actuated to pull the seed tube vertically away from surface **20.** The pulling speed is set so that surface tension will cause the film to adhere to the seed tube long enough for crystallization to occur due to a drop in temperature at the seed tube-liquid film interface. This drop in temperature occurs because of movement of the seed tube away from surface **20,** i.e. because the solid-liquid interface is moved to a relatively cooler region. The pulling speed also must be set so that if initially the film **40** does not fully cover surface **20** so as to extend into contact with wires **30,** surface tension will cause the film to spread radially until it fully covers surface **20** (see FIG. **3**). In growing monocrystalline alpha-alumina, the pulling speed initially is set at about 0.1 in./min. until the film fully covers the end surface **20** after which it is preferably increased to as much as 1.0 in./min. It is to be noted that the pulling speed of the tubular seed and the temperature of the film control the film thickness which controls the rate of film spreading. Increasing the temperature of surface **20** (and hence the temperature of the film) and increasing the pulling speed (but short of the speed at which the seed will pull clear away from the film) each have the effect of increasing the film thickness.

As seed tube **38** is pulled, crystal growth will occur at all points along the horizontal expanse of the film, with the result that a tubular monocrystalline extension is formed on the seed tube. Since molybdenum is wet by molten alumina, the film will wet wire **30** and at the solid-liquid interface alumina will feeze around the wire so that the wire is embedded in and gripped by the monocrystalline extension that is grown as illustrated at **41** in FIG. **3.** Consequently as pulling is continued, the wire **30** is pulled up with the crystalline extension formed on the end of the seed tube, so that additional accretions of crystal growth form a monocrystalline body around successive portions of the wire as shown at **42** in FIG. **4.** The film consumed by the crystal growth is replaced by additional melt which is supplied by the capillaries **24.** The process may be continued until the tubular extension has grown to a desired length or until the supply of melt has been depleted to the point where the bottom ends of the capillaries are no longer trapped or until all of the wire has been used, whichever event occurs first. The growth process may be terminated at any point by increasing the pulling speed enough to cause the growing body to pull free of the melt film **40.** Any unused wire is pulled out of the die with the growing body when the latter is pulled free. Once growth has been terminated, the furnace is shut down and the seed tube removed from the furnace. Thereafter the monocrystalline extension is severed from the seed tube by means of a diamond cutter and then processed to effect removal of the embedded wire. Removal of the embedded wire may be achieved by burning the wire in an oxygen atmosphere. A molybdenum wire can be removed by oxidizing it at about 900°C. Removal of the wire by burning it is practical only where the product is cut into relatively short lengths, e.g. up to about one-half to one inch long. Preferably removal of the wire is effected by dissolving it in a solvent medium that does not attack alumina. One suitable solvent consists of equal parts of water, HF. and HNO_3. Although dissolution may be done at room temperature, it is preferred to do it at elevated temperatures to save time. It is to be noted that boiling phosphoric acid is not suitable as a solvent since it attacks alumina.

As noted above, it also is possible to practice the invention starting with a seed in the form of a filament or ribbon. This mode of practising the invention is shown in FIGS. **5** to **8** using the same die as shown in FIG. **2.** Initially a seed in the form of a monocrystalline filament **43** is brought into contact with the hot surface **20** and held there long enough for some of it to melt and form a small area liquid film **44** that connects with the melt in one of the capillaries **24.** Thereafter the filament seed **43** is pulled at a speed at which the surface tension will cause the film to exapnd laterally over the surface **20.** As the film begins to spread, it is augmented by additional melt supplied by the capillary. The crystal growth **46** on the end of the filament also expands laterally with the film. The film spreads radially inward and also circumferentially on surface **20** (see FIG. **6**) until it completely surrounds the projecting end of wire **30,** and the crystal growth **46** expands in a corresponding manner. The wire **30** begins to be pulled upward as soon as sufficient crystal growth has formed around it to exert a gripping force thereon. This upward movement is apparent from a comparison of FIGS. **6** and **7.** In FIG. **7** the crystal growth **46** has expanded horizontally with film **44** until at the liquid-solid interface its o.d. is substantially the same as the o.d. of rod **18** and the film is being fed melt by all of the capillaries. Once the growth has expanded to the full size of surface **20,** it may be continued so as to form an elongate monocrystalline tube surrounding wire **30** as shown at **48** in FIG. **8.**

The same results may be achieved using a die similar to that shown in FIG. **2** but omitting capillaries **24.** Such a die is shown in FIG. **9** at **14A.** In this case the rod **18A** is formed with an axially extending center bore **22A** that is oversize with respect to wire **30** by an amount such as to leave a gap between the wire and rod **18A** that will allow melt to rise to the top of the bore by action of capillary rise from the reservoir of melt in the crucible. Guide means (not shown) may be provided at the bottom end of rod **18A** to center the wire in bore **18A.** Using the die of FIG. **9,** growth may be achieved in the same manner as described above in connection with FIGS. **1–4,** provided that initially melting of the seed is accomplished so as to provide on surface **20** a film of melt that is connected to the melt in bore **22A.**

Still other modifications of the process are possible. For example, it is possible to use a flat or ribbon-like wire instead of a round wire, in which case the product will have a non-circular capillary bore. This is achieved by using a die assembly of the type shown in plan view in FIG. **10.** In this case the die assembly consists of two rods **50A** and **50B** of semicircular cross-section mounted in a disc **52** corresponding in function to disc **16.** Rods **50A** and **50B** are formed with matching longitudinally extending slots in their adjacent faces. The slots are shaped so as to provide a rectangular passageway sized to accommodate and guide a wire **54** of rectangular cross-section and two smaller rectangular passageways **56,** one on each side of wire **54,** that function as capillaries. Typically the wire ribbon may measure 0.006×0.100 inch in cross-section and the passageways **56** have a width (the horizontal dimension in FIG. **10**)

in the order of 0.002 inch. Alternatively or in addition to passageways **56**, rods **50A** and **50B** may be formed with round axially extending capillaries as shown in phantom at **58**.

FIG. **11** shows still another modification. In this case, the die assembly comprises a circular rod **18B** that is like rod **18** except that it extends to the bottom of crucible **2** and has side openings **60** to admit melt to the capillaries **24**. Additionally the bottom walls of the crucible and the susceptor **6** are formed with center holes **62** and **64** respectively through which the wire **30** may be fed into the axial bore **22** of rod **18B**. The bottom end of rod **18B** is welded to the bottom wall of the crucible so as to prevent the melt from escaping via hole **62** and disc **16** is removable for addition of melt material in the crucible. The crystal growth process using the die assembly of FIG. **11** is the same as that described above in connection with FIGS. **1'–4**, except that the wire **30** is fed in from the bottom. Of course, the die **18B** may be made like that of FIG. **10** so as to accommodate a flat or ribbon type wire.

Following is a detailed example of how to practice the invention.

EXAMPLE

A molybdenum crucible as shown in FIG. **1** and having an internal diameter of 1 ¼ in., a wall thickness of about 3/16 in., and an internal depth of about **1** in. is positioned on rods **8** in susceptor **6** mounted in a furnace in the manner shown in FIG. **1** of U.S. Pat. No. 3471266. Disposed in the crucible is a molybdenum die assembly constructed generally as shown in FIG. **1**. The rod **18** has four capillaries **24** spaced uniformly about its center bore **22**. The dimensions of rod **18** are as follows: a rod diameter of about 0.15 inch, a rod length such that its upper end projects about 1/16 inch above the crucible and its lower end terminates approximately 1/16 inch above the bottom end of the crucible. The four capillaries each have a diameter of about 0.03 inch and the center bore has a diameter of about 0.004 inch. The crucible is filled with substantially pure polycrystalline alpha-alumina and a monocrystalline alpha-alumina tube **38** grown previously by the EFG technique is mounted in the holder of the crystal pulling mechanism. The tube **38** is cylindrical and was grown so that the *c*-axis of its crystal lattice extends parallel to its geometric axis. Additionally tube **38** has an outside diameter identical to the outside diameter or rod **18** and a wall thickness of about 0.015 inch. Tube **38** is supported by the crystal pulling mechanism so that it is aligned axially with rod **18**. A molybdenum wire **30** having a diameter of about 0.002 inch is inserted into the central bore **22** of rod **18**. The wire is passed under the two guide pins **26** and **28** and extends up through the aperture **32** in the disc **13**. The wire is continuously fed from a spool above which is not shown.

With the crucible **2** and susceptor **6** mounted in the furnace, the furnace enclosure is evacuated and filled with argon to a pressure of about one atmosphere which is maintained during the growth period. Then the induction heating coil of the furnace is energized and operated so that the alumina in the crucible is brought to a molten condition (alumina has a melting point in the vicinity of 2050°C) and the surface **20** is brought to a temperature of about 2070°C. As the solid alumina is converted to the melt **4**, columns of the melt rise in and fill capillaries **24**. Each column of melt rises until its meniscus is substantially flush with the top surface **20** of rod **18**. After affording time for temperature equilibrium to be established, the pulling mechanism is actuated and operated so that the tube **38** is moved down into contact with the upper surface **20** of the die assembly and allowed to rest in that position long enough for the bottom end of the tube to melt and form film **40**. Initially the film **40** extends from the outside edge of the surface **20** to a point in line with the inner surface of the seed tube **20**, as shown in FIG. **2**. After about sixty seconds, the tube **38** is withdrawn vertically at the rate of about 0.1–0.2 inch per minute. As the tube is withdrawn, crystal growth occurs on the seed and the film begins to spread inwardly over the surface **20** due to its affinity with the newly grown material on the seed tube and the film's surface tension. The film spreads inwardly until it wets the projecting end of the wire **30**. As the seed tube **38** is pulled vertically, the film's surface tension also causes additional melt to flow out of the capillaries and add to the total volume of film.

Since the film functions as a growth pool of melt, as the film spreads out over the surface **20**, the crystal growth also expands horizontally. At the aforesaid pulling speed growth propagates vertically throughout the entire horizontal expanse of the film, with the result that the growing crystal begins to grow radially inward as shown in FIG. **3** until after about **3** minutes, it conforms in cross-sectional area and shape to the surface **20** and abuts and grips the wire **30**. As growth continues, the newly grown crystal being pulled pulls the wire **30** up through the bore **22**, with the result that successive accretions of crystal growth surround successive sections of the wire **30**. After about **10** minutes of pulling the tube with crystal growth occurring as illustrated in FIG. **4**, the pulling speed is increased to as much as 1.0 inch per minute. The pulling speed is maintained at that level until the desired length of crystal has been grown. Once the desired length has been pulled, the pulling speed is immediately increased to about 2.0 inch/min. whereby the grown monocrystalline body pulls free of the film **40**. Thereafter the furnace is cooled, the wire connecting the die and crystal is severed, and the seed tube **38** with the grown crystal thereon is retrieved from the furnace. The grown crystal has a reasonably smooth cylindrical outer surface and in cross-section has the same configuration as the surface **20** of the rod **18**. The grown crystal is found to be essentially monocrystalline and a crystallographic extension of the crystal lattice of the seed tube **38**. The grown crystalline body is then cut into short lengths of about one-half inch length by means of a diamond cutter and these short lengths are immersed in a bath consisting of equal parts of water, HF and HNO_3 maintained at a temperature of about 100 °C until the molybdenum wire has been dissolved out of each piece.

It is to be noted that if initially growth occurs on the seed tube but the film **40** does not immediately begin to spread inwardly toward the wire **30**, steps may be taken to force the melt film to spread as desired. This can be accomplished by adjusting the temperature of the film or by adjusting the pulling speed. Preferably the temperature of the surface **20** is held constant and the pulling speed adjusted until spreading of the film is observed.

It is to be noted also that after the melt film has fully covered the surface **20** and growth begins to occur around the wire **30**, if the operating temperature (as

determined by the average temperature of film **40**) is held constant close to but slightly above the melting point of the material to be grown, the pulling speed may be varied within limits (depending upon the operating temperature) without any substantial change in the cross-section of the grown crystal. Similarly if the pulling speed is held constant, the operating temperature may be varied substantially (e.g., a change of as much as 15°–30° with respect to the melting point of alumina) without any substantial change in the cross-section of the grown crystal.

The procedure followed in the foregoing example may also be followed in growing capillary tubes using the apparatus of FIGS. **9–11.** In the case of the apparatus of FIG. **9,** by way of example, if the wire **30** has a diameter of 0.002 inch, the bore **22** A will have a diameter of about 0.010 inch. It is to be noted further that the invention may be used to grow capillary tubes having a substantially larger o.d. than the capillary tube produced according to the foregoing example. However, where the growing tube has a relatively large o.d. and wall thickness, it may be necessary to increase the rate of heating slightly so that the temperature of the upper end surface **20** of the die assembly before it is contacted by the seed tube is greater than that normally required to be maintained for satisfactory growth. This higher temperature offsets the heat sink effect of the tube which may cause the film of melt to have a lower average temperature than expected. Unless this heat sink effect is offset by an increase in the rate of heating, the seed tube **38** may not melt to form the film **40** or the film may not spread rapidly over the surface **20,** unless the pulling speed is adjusted to compensate for the heat sink effect.

It is to be noted that the same process may be used to grow tubes having more than one capillary therein. This is accomplished by providing a plurality of parallel spaced bores like bore **22** in the die assembly and feeding individual wires like wire **30** up through each bore.

It is to be noted also that the invention may be used in growing capillary tubes of other cross-sectional shapes, e.g., capillary tubes having rectangular, square, etc., outside configurations or capillary tubes having capillary bores of rectangular, square, or other cross-sectional configurations. Thus by using a die assembly with a rod **18** having a film supporting surface as at **20** with a square exterior configuration, it is possible to grow a capillary tube having a square cross-section and a circular capillary bore onto the seed tube **38.** It is to be noted also that the seed tube **38** need not be circular in cross-section, but may be square, rectangular, etc. Regardless of the cross-sectional configuration of the seed tube, the newly grown crystal will have a cross-section with a configuration conforming to the configuration of the film from which it is grown, the film conforming to the shape of the upper end surface of the die assembly.

An important advantage of the invention is that it is applicable to crystalline materials other than alumina. It is not limited to congruently melting materials and encompasses growth of materials that, for example, solidify in cubic, rhombohedral, hexagonal, and tetragonal crystal structures, including barium titanate, yttrium aluminum garnet, and lithium niobate mentioned above. With respect to such other materials, the process is essentially the same as that described above for alpha-alumina, except that it requires different operating temperatures because of different melting points and the wire **30** may be made of a material other than what may be used when the melt is alumina. The essential point is that the wire **30** must be made of a material that will be wet by the melt film and will not react with the die or melt at the required operating temperatures. Additionally, certain minor changes obvious to persons skilled in the art may be required in the apparatus, e.g., different crucible and die materials may be required in order to avoid reaction between the melt and the crucible and die assembly.

Laue X-ray back reflection photographs of alpha-alumina crystal growth produced according to the foregoing invention reveals that the crystal growth usually comprises one or two, and in some cases three or four crystals, growing together longitudinally separated by a low angle (usually within 4° of the c-direction) grain boundary.

Similar crystal structure occurs when growing other materials such as barium titanate, etc. Therefore, for convenience and in the interest of avoiding any suggestion that the crystal growth is polycrystalline in character, it is preferred to describe it as "substantially monocrystalline", it being understood that this term is intended to embrace a crystalline body that is comprised of a single crystal or two or more crystals, e.g., a bicrystal or tricrystal, growing together longitudinally but separated by a relatively small angle (i.e., less than about 4°) grain boundary. The same term is used to denote the crystallographic nature of the seed tube.

With respect to the die assembly, it is to be understood that the term "end surface" is intended to cover the effective film-supporting surface of the die, whether the die is made as a single piece or as two pieces, and the term "capillary" is intended to denote a passageway that can take a variety of forms, such as the discrete bores **24.** The term "effective film-supporting surface" denotes the end surface of the die, e.g. surface **20,** as it would appear if the capillary opening or openings were omitted since when a film fully covers the end surface it extends over the capillary openings as shown in FIGS. **2–4.**

The invention offers another advantage in addition to making possible the production of small monocrystalline capillary tubes of high temperature resistant materials, namely, production of strong composites. In this connection it is to be noted that if the process is carried out so that crystal growth occurs around a plurality of wires or filaments simultaneously and if removal of the embedded wires is not attempted, the product of the invention constitutes a composite consisting of one or more wires or filaments of one material embedded in a monocrystalline matrix of another material.

It is to be noted that the parts shown in the drawings have not been drawn to exact scale and that the size of the bore **22,** for example, has been exaggerated in relation to the size of capillaries **24** for convenience of showing the wire **30.**

What is claimed is:

1. Method of producing an elongate substantially monocrystalline body having a passageway therein comprising inserting one end of an elongate wire through a hole in a substantially horizontally extending surface that has a predetermined edge configuration, establishing on said surface a liquid film of a selected material that has a lower melting point than said wire and is crystalline when in solid form, growing a substan-

tially monocrystalline body of said material from said film so that said body surrounds and grips said wire, pulling said body vertically away from said film as it grows vertically whereby successive portions of said wire move upwardly through said hole and are gripped by successively grown portions of said body, continuously feeding additional quantities of said material in liquid form to said surface via an opening therein to replenish and maintain said film, terminating further crystal growth on said body after said body has grown to a substantial length, and thereafter removing the wire from said body so that the space in said body formerly occupied by said wire forms an elongate open passageway.

2. Method of claim **1** wherein said wire and said hole are both circular in cross-section.

3. Method of claim **1** wherein said wire is a flat ribbon.

4. Method of claim **1** wherein said material is alumina and said surface and said wire are made of a material from the class consisting of molybdenum, tungsten, iridium and rhenium.

5. Method of claim **1** wherein said additional quantities of said material are supplied to said surface from a reservoir of melt of said material disposed below the level of said surface.

6. Method of claim **1** wherein said additional quantities of said material are supplied to said surface via a capillary opening into said surface.

7. Method of claim **1** wherein said additional quantities of said material are supplied to said surface via said hole.

8. Method of producing a substantially monocrystalline body comprising inserting at least one wire through a hole in a substantially horizontal surface that has a predetermined edge configuration, establishing on said surface a liquid film of a selected material that has a lower melting point than said wire and is crystalline when in solid form and growing a substantially monocrystalline body of said material from said film with said body surrounding and gripping said at least one wire, pulling said body vertically away from said film at a speed consistent with the rate of crystal growth in a vertical direction so that successive portions of said at least one wire are surrounded and gripped by successive accretions of crystal growth on said body, feeding additional quantities of said material in liquid form to said surface via a hole in said surface to replenish and maintain said film as said body is pulled vertically, and terminating crystal growth after said body has grown to a desired length.

9. Method according to claim **8** wherein said material is alumina and said at least one wire is made of a material that is wet by alumina.

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