

[54] **NON-WETTING AID FOR GROWING CRYSTALLINE BODIES**

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[58] Field of Search **23/301 SP, 273 SP**

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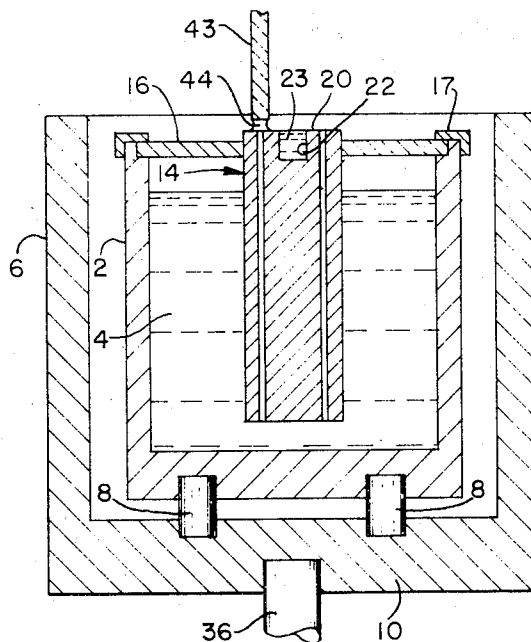
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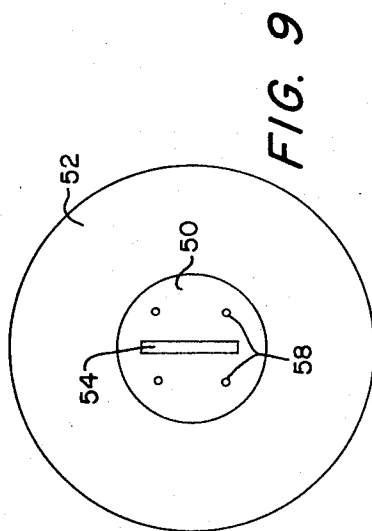
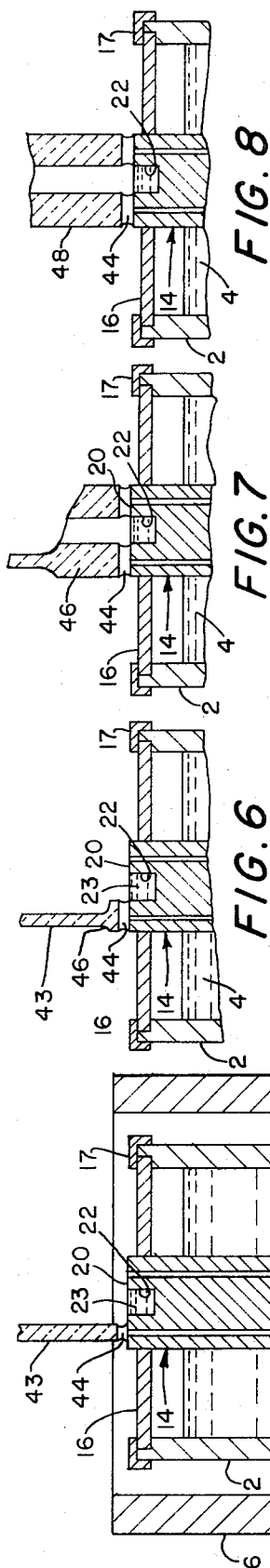
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[57] **ABSTRACT**

The invention is a method and apparatus for growing crystalline bodies from the melt. Monocrystalline bodies of a material such as alumina are grown from a melt on a novel "die" assembly which determines the shape of the crystalline body.

12 Claims, 11 Drawing Figures





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NON-WETTING AID FOR GROWING CRYSTALLINE BODIES

This invention relates to growing crystals and more particularly to a modification of the EFG process and to novel dies for use in such process.

The term "EFG" stands for edge-defined, film-fed, growth and designates a process for growing crystalline bodies from a melt, details of which are described in U.S. Pat. No. 3,591,348 of Harold E. LaBelle, Jr., issued July 6, 1971 for Method of Growing Crystalline Materials.

In the EFG process the shape of the crystalline body that is produced 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, although it does not function in the same manner as a die. By this process a variety of complex shapes can be produced commencing with the simplest of seed geometries, namely, a round small diameter seed crystal. The process involves growth on a seed from a liquid film or film 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 of the die's end surface, a continuous hole may be grown in the crystalline body by providing in that surface a blind hold, i.e. a 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 a film around the hole to fill in over that 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 of liquid which is constantly replenished.

The primary object of this invention is to improve upon the EFG process and to provide novel apparatus for use in such process.

Specific objects of this invention are to improve upon existing EFG processes and apparatus for growing relatively large diameter tubular bodies, e.g. tubular bodies for use as envelopes for high intensity vapor lamps, and relatively long small diameter capillary tubes.

With the EFG process, growth of relatively large size tubular bodies is achieved using a die having an annular film supporting surface, with a blind hole defining the inner edge of the film-supporting surface. Occasionally

in initiating or terminating crystal growth, melt is spilled over into the blind hole, thereby making it impossible to grow a tubular body and occasionally making it necessary to provide a new die at extra cost of money and time. A similar problem has been encountered when attempting to grow relatively long small diameter capillary tubes by existing EFG processes. Ceramic capillary tubes are useful for various purposes, e.g. as thermocompression 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. Prior to the EFG process, relatively short, e.g. one-fourth inch long, monocrystalline ceramic capillary tubes were possible by forming a hole in and shaping a monocrystalline boule, but no practical way existed for forming in one step a substantially monocrystalline tube of alumina or other high temperature materials having small internal diameters, e.g. bores with a diameter in the order of about 0.006 inch. Attempts to grow relatively long small diameter capillary tubes by the EFG process as above described were not 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. Subsequently, this problem of liquid filling in the blind hole was overcome by an improvement in the EFG process whereby elongate monocrystalline bodies were grown about small diameter; high-temperature wires or filaments so as to form high strength composites, with the small wires or filaments subsequently being removed so as to leave monocrystalline bodies with capillary size openings therein. While such improvement makes it possible to produce relatively long small diameter capillary tubes of materials such as alumina, it is not fully satisfactory from a cost standpoint due to the additional step of removing the wires or filaments from the formed composites. Thus a specific object of this invention is to grow small diameter tubes without need for wires or filaments as above described. Still other objects will be obvious from the following detailed specification.

Described briefly, this invention consists of providing a region or regions of non-wetting material on the film-supporting surface of an EFG die. Melt is fed up to the surface of the die or forming member through one or more capillaries in the die that leads to a reservoir of melt. Then a film of melt that connects with the melt in the capillaries is formed on the film-supporting surface of the die 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 except for those regions characterized by non-wetting material 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 but around those regions characterized by said non-wetting material. The resulting product is a substantially monocrystalline body having a shape determined by the edge configuration of the die or forming member and any regions of non-wetting material. The product can be made to have one or more elongate holes running parallel to the axis of said product by suitable arrangement of one or more regions of non-wetting material on the surface of the die or forming member. If desired, the outside shape of the body can also be determined by suitable arrangement of non-wetting material around

the outer margin of the film-supporting surface of the die.

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 growing a tubular body according to this invention;

FIGS. 2-4 are fragmentary vertical sectional views illustrating how a monocrystalline tubular body 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 plan view of a second form of die for use in growing a crystal body in accordance with the present invention;

FIG. 10 is a plan view of still another form of die for use in growing a crystal body according to the present invention; and

FIG. 11 is a fragmentary vertical sectional view of still another form of die for use in practicing the invention.

The present invention may be used to produce monocrystalline bodies of the character described made of any one of a variety of materials that solidify in identifiable crystal lattices. By way of example, the material may be alumina, ruby, beryllia, spinel, barium titanate, lithium niobate, yttrium aluminum garnet, copper or germanium. 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 drawings 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 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 die member in the form of 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 cru-

cible. Rod 18 has a flat, substantially horizontal, top end surface 20, a region of non-wetting material in the form of a well 22 formed in the upper end of the rod and filled with a pool of non-wetting material 23, 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. The well 22 has a cross-sectional size and shape corresponding to the size and shape of the hole desired in the crystal body being grown. Preferably the capillaries 24 are uniformly spaced about the axis of rod 18.

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 growth 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. 3,471,266 issued Oct. 7, 1969 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. 3,471,266.

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 nontubular seed. Thus it is possible to start with an alpha 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.

Referring now to FIGS. 1-4, the following description illustrates how an alpha alumina 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. 3,471,266 in which an argon atmosphere is maintained and the crucible and capillaries 24 are filled with an alumina melt. Assume also that a seed in the form of a previously grown sapphire tube 38 having an internal diameter equal to the diameter of well 22 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 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). The central axis of seed tube 38 should be aligned with the central axis of region 22. 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 also that before the end of tube 38 is melted to form film 40, the melt in each capillary has a concave menis-

cus 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, surface tension will cause the film to spread radially until it fully covers surface 20 (see FIG. 3). No film, however, will spread over the well 22 since the material 23 therein is not wet by the film material. 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 except over the material 23 in well 22, with the result that a tubular monocrystalline extension is formed on the seed tube. Consequently as pulling is continued, additional accretions of crystal growth form a longer and longer monocrystalline body. 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. 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. 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.

As noted above, it also is possible to grow a tubular body starting with a seed in the form of a filament or ribbon. This mode of practicing the invention is shown in FIGS. 5 to 8 using a die similar to the one 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 of liquid film 44 that connects

with melt in at least one of the capillaries 24. Then the seed filament 43 is withdrawn at a pulling speed such as to cause the film 44 to spread radially and also circumferentially on the surface 20. As the film spreads crystal growth occurs along the entire expanse of the film so that the growing crystal expands laterally as shown at 46 in FIG. 6. As growth proceeds additional melt flows up through the die to replenish the film and the latter continues to spread until it fully covers surface 20 (except over well 22) and is being fed melt by all of the capillaries. The crystal growth 46 expands in a corresponding manner until, as shown in FIG. 7, its o.d. is substantially the same as the o.d. of rod 18 and its i.d. is the same as the o.d. of well 22. Once the growth has expanded to the full size of surface 20, it is continued so as to form an elongate monocrystalline hollow rod as shown at 48 in FIG. 8.

As is believed to be obvious to persons skilled in the art, the invention as described in connection with FIGS. 1-8 may be used to grow small capillary tubes or large size tubes suitable, for example, as lamp envelopes. the cross-sectional size of the body that is grown depends upon the size of the effective filmsupporting area of the surface 20. Thus by making the cavity 22 small, it is possible to grow a tube with a capillary size bore. On the other hand, if the cavity 22 is relatively large in diameter, the product will have a relatively large through bore. The wall thickness of the tube is determined by the difference between the outside diameter of rod 18 and the diameter of cavity 22.

Other modifications of the invention are possible. For example, it is possible to use a non-circular region of nonwetting material in surface 20, 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. 9. In this case the die assembly consists of a rod 50 of circular cross-section mounted in a disc 52 corresponding in function to disc 16. The upper end of the rod has a well or cavity 54 that is filled with a non-wetting material and is shaped in a rectangular configuration. Axially extending capillaries 58 are provided in rod 50 to supply melt to the surface thereof.

In another modification of the invention the external shape of the crystal being formed can be defined by an appropriately shaped region of material which is not wetted by the crystal being grown. 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 a rod 60 of circular cross section mounted in a disc 62 corresponding in function to disc 16. A cavity or well 64 having a shape and dimension corresponding to the desired shape and dimension of the crystal being grown is provided in the surface of rod 60. In this particular case the cavity 64 is in the shape of a square ring that completely encircles axially extending capillaries 68 in rod 60 which supply melt to the surface thereof. Cavity 64 is filled with a selected material that is not wet by the melt. Region 70 (shown in phantom) comprising a second cavity (that may or may not be filled with a non-wetting material) may also be provided in the surface of rod 60 when it is desired to also form a hole in the crystal. It is believed to be obvious that the die assembly of FIG. 10 is used to grow a body of square cross-section with the sides of the body conforming substantially to the length of the inside edge of one side of cavity 64,

and that such body will have a central bore if the die is provided with a cavity as shown at 70.

Following is a detailed example of how to grow a tube according to this invention.

EXAMPLE

A molybdenum crucible as shown in FIG. 1 and having an internal diameter of $1\frac{1}{4}$ inch, a wall thickness of about three-sixteenths 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. 3,471,266. 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 centrally positioned circular well 22. The dimensions of rod 18 are as follows: a rod diameter of about 0.75 inch, a rod length such that its upper end projects about one-sixteenth inch above the crucible and its lower end terminates approximately one-sixteenth inch above the bottom end of the crucible. The four capillaries each have a diameter of about 0.03 inch and the circular well 22 has a diameter of about 0.40 inch and a depth of about 0.30 inch. The well 22 is prefilled with pure tin (which is a non-wetting material relative to molten alumina) and the crucible is filled with substantially pure polycrystalline alumina powder before the die assembly is installed in the crucible. 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 of rod 18 and a wall thickness of about 0.10 inch. Tube 38 is supported by the crystal pulling mechanism so that it is aligned axially with rod 18.

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. The tin in the well 22 (which has a melting point of only about 232°C) is also brought to a molten condition. 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 and 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 except the film will not spread over the region occupied by the molten tin since molten alumina will not wet molten tin. 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, i.e., the crystal has a round shape with a hole in the center. 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 0.3 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, 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 dimensions of the cross-section of the grown crystal are as follows: an outer diameter about the same as that of the seed tube, and an inner diameter substantially the same as the diameter of cavity 22. The grown crystal is found to be essentially monocrystalline and a crystallographic extension of the crystal lattice of the seed tube 38.

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, 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.

It is to be noted further that the invention may be used to grow tubes having a substantially larger o.d. than the 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 bore therein. This is accomplished by providing in the die assembly a plurality of regions of nonwetting material.

The procedure set forth in the foregoing example may also be used to grow small diameter capillary tubes, e.g. tubes with an i.d. of 0.01 inch.

As noted above, the cavity 22 is prefilled with pure tin. If the cavity is relatively large in diameter, the tin may be initially introduced in particle or solid form in an amount sufficient to fill the cavity after being melted and then resolidified. If the well 22 is small in diameter as when growing a capillary tube, the cavity 22 is initially filled by inserting a small diameter tin wire in the well and melting it until the well is filled. Preferably the wire is sized so as to permit it to be inserted to the full depth of the cavity and has an internal length greater than the depth of the cavity so that there is enough tin to displace whatever gases are expelled from the cavity when the tin is melted. The tin is heated high enough to expel all gases that may cause occlusions in that growing crystal body. Once the cavity 22 has been fully filled with molten tin and all gases expelled, the tin is cooled so that it will solidify and the die is then ready for use as described in the foregoing example.

It is to be noted also that the invention may be used in growing tubes (whether of capillary size or larger) of other cross-sectional shapes, e.g., tubes having rectangular, square, etc., outside configurations or tubes having one or more 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-section 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 effective filmsupporting surface of the die assembly. In each case the nonwetting material 23 obviates the possibility of the undesired fill-in of the cavity 22 by the liquid film.

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 ruby, spinel, beryllia, barium titanate, yttrium aluminum garnet, lithium niobate, germanium and copper. With respect to such other materials, the process is essentially the same as that described above for alphaalumina, except that it requires different operating temperatures (because of different melting points), dies made of different materials, and different non-wetting materials. For example, where a germanium crystal is being grown the die may be made of tungsten and the non-wetting material may be carbon; and, in the case of copper, the die may be

made of molybdenum and the non-wetting material may be alumina.

It should be understood also that the non-wetting material does not have to be molten at the operating temperature, that is, the non-wetting material 22 can be a solid. In the latter case the non-wetting material may be located in a well or cavity so as to be substantially flush with the surface of the die or it may extend above the surface of the die. Furthermore, it need not be disposed in a well or cavity. Thus the non-wetting material may be in the form of a thin solid film attached to the upper end surface of the die and applied by electroplating, vapor deposition, or other suitable technique known to persons skilled in the art. This form of the invention is shown in FIG. 11 where a layer of a solid non-wetting material in the shape of a round disc 74 covers the center area of the upper surface 20 of the die member 18 and another layer of the same material in the form of a circular annulus 76 is disposed concentric to the disc 74. This die is suitable for growing a tubular body 78, with growth occurring from a melt film 80 that is replenished via capillaries 24 and which overlies the upper surface only in the area between disc 74 and annulus 76. The essential thing is that the non-wetting material be disposed so as to define a region with a configuration corresponding to a desired configuration for the product. In this respect its function is the same as the edge of a blind hole and the outer edge of the upper surface of the die. Of course, whether a solid or liquid, the non-wetting material must be one which will not be wet by the melt film and will not react with the die or melt at the required operating temperatures.

Of course it is not necessary for the die member 18 to be supported by the disc 16. Instead the disc 16 may be separable from the die member and rest on the crucible so as to function as a crucible cover and a radiation shield for the melt 4, while the die member be otherwise secured to the crucible. Thus the die member may rest on the bottom of the crucible and have side ports at its bottom end to permit inflow of melt, as described in U.S. Pat. No. 3,591,348.

Laue X-ray back reflection photographs of alphaalumina 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 crystal, growing together longitudinally separated by a low angle (usually with 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 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, which may comprise only a part of the end surface of the die in the case where the outside edge of the filmsupporting surface is determined by a region of non-wetted material rather than by the perimeter of the die, and the term "capillary" is intended to denote a pas-

sageway 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.

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 capillaries 24, for example, has been exaggerated in relation to the size of the cavity 22 for convenience of illustration.

What is claimed is:

1. A method of producing an elongate substantially monocrystalline body of a first selected material having a substantially constant cross-section of predetermined shape, said method comprising establishing a liquid film of said first selected material on a substantially horizontally extending surface of a second solid material that is wettable by said first selected material and has a predetermined configuration at least partly defined by a third liquid or solid material that is not wetted by said film so that said film terminates at the boundary of said third material, growing a substantially monocrystalline body of said first material from said film and pulling said body vertically away from said film as it grows, and replenishing said film by feeding an additional quantity of said first material in liquid form to said surface via at least one opening in said surface.

2. Method of claim 1 where said crystalline material is alumina and said non-wetting material is tin.

3. Method of claim 1 wherein said third material is surrounded by said surface.

4. Method of claim 1 wherein said third material surrounds said surface.

5. Method of claim 1 wherein said third material is in liquid form.

6. Apparatus for growing a monocrystalline body of

a selected material from a melt of said material comprising a die having a substantially horizontally extending top end surface with a predetermined edge configuration, said surface material that is wettable by the melt and further characterized by at least one region consisting of a material in liquid or solid form that is not wetted by said melt, and a capillary in said die leading down from said top end surface outside of said region for feeding melt to said top end surface.

7. Apparatus as in claim 6 wherein said region of non-wettable material is substantially circular in cross-section.

8. Apparatus as in claim 6 wherein said region of non-wettable material is substantially flush with said top surface of said die.

9. Apparatus as in claim 6 wherein said region of nonwetting material extends above said top surface of said die.

10. Apparatus as in claim 6 wherein said top end surface is made of molybdenum and said non-wetting material is tin.

11. Apparatus for use in growing a monocrystalline body of a first material from a melt of said first material comprising:

a crucible for containing a supply of said melt; and a die disposed in said crucible, said die comprising a second material that is wettable by said melt and a third material that is not wettable by said melt, said die having a top end surface for supporting a film of said melt, said top end surface being made of said second material and having a predetermined edge configuration that is defined at least in part by said third material, and a passageway in said die leading down from said top end surface for feeding melt from said supply to said top end surface.

12. Apparatus according to claim 11 wherein said third material has a melting point below the melting point of said second material.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,853,489

Dated December 10, 1974

Inventor(s) John S. Bailey

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

Column 12, Claim 6, Line 4, after "surface" insert

--being a--.

Signed and sealed this 18th day of February 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks