

- [54] **APPARATUS FOR GROWING CRYSTALLINE BODIES FROM THE MELT**
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abandoned.
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65/87
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- [58] Field of Search **23/273 SP**, 301 SP

References Cited

UNITED STATES PATENTS

- 2,793,103 5/1957 Emeis 23/273

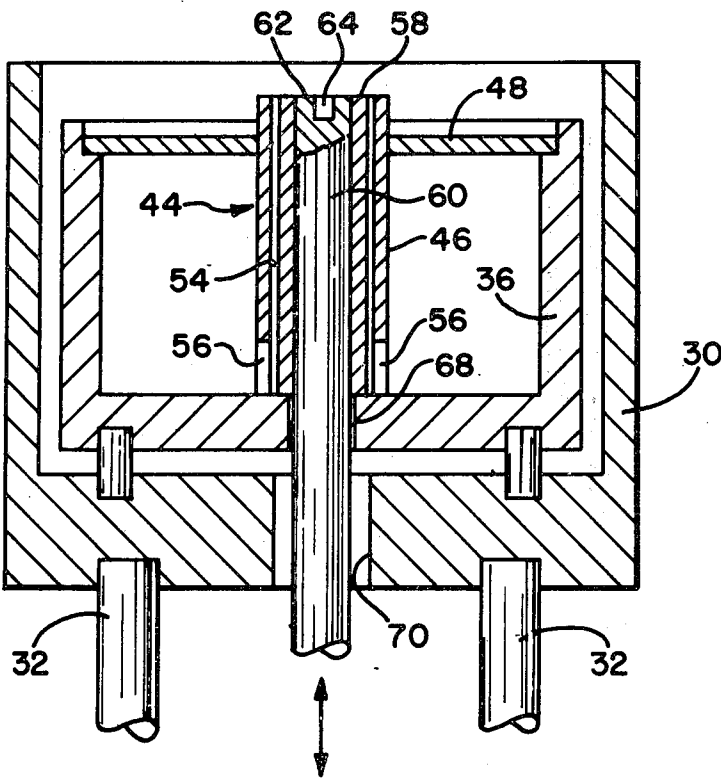
2,893,847	7/1959	Schweickert et al.	23/273
3,015,592	1/1962	Leopold	23/273
3,198,606	8/1965	Lyons	23/273
3,241,925	3/1966	Cakenberghe	23/273
3,716,345	2/1973	Grabmaier	23/273

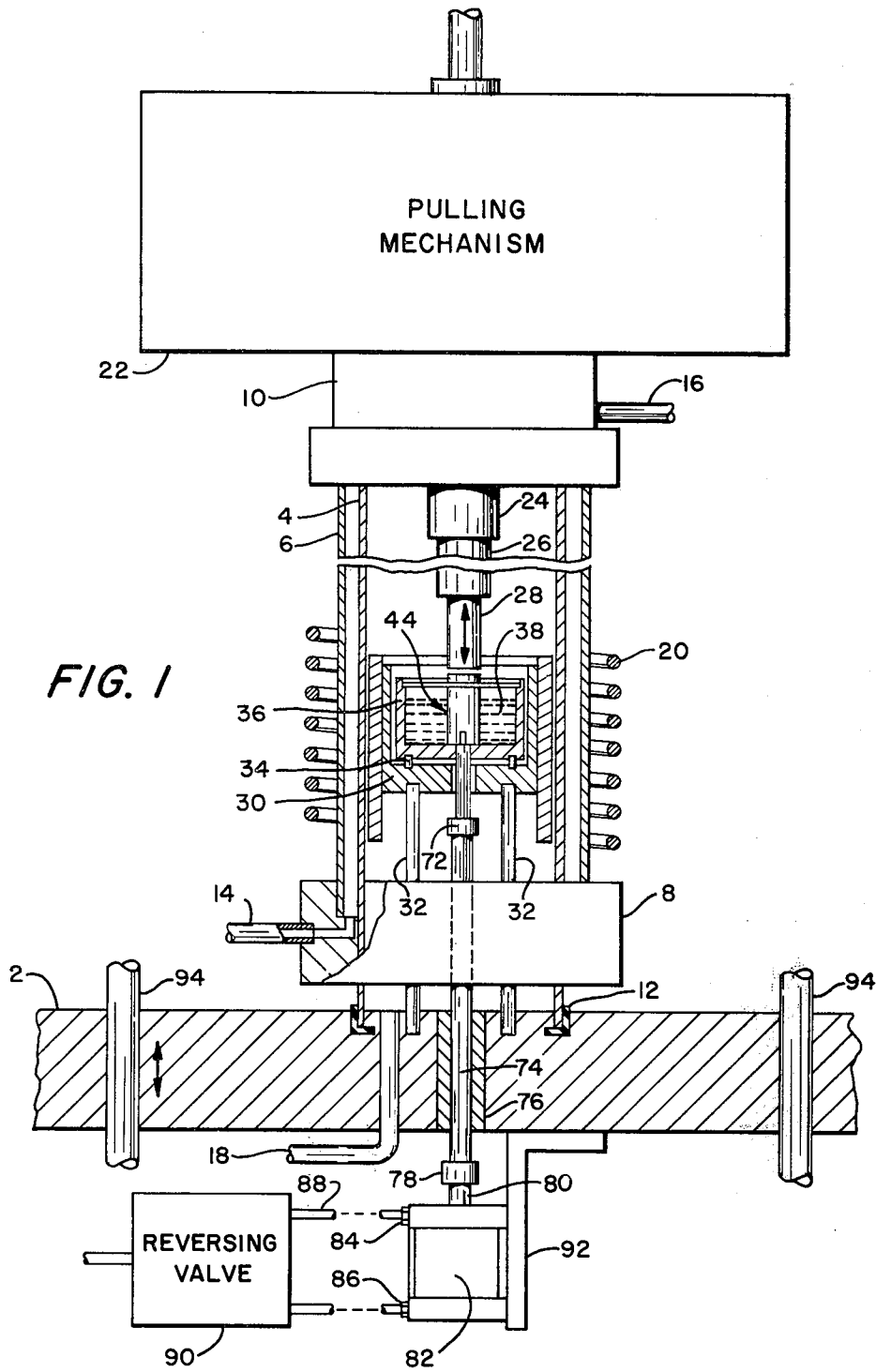
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[57] **ABSTRACT**

The invention is an improved apparatus for producing monocrystalline bodies of alumina (or other materials) that are characterized by varying cross-sections, for example, a sapphire tube having an internal flange. The apparatus comprises a novel die arrangement adapted to support a thin film of melt from which the crystalline body is grown, the die being adjustable to change the configuration of the film and thereby vary the shape of the body being grown.

12 Claims, 8 Drawing Figures





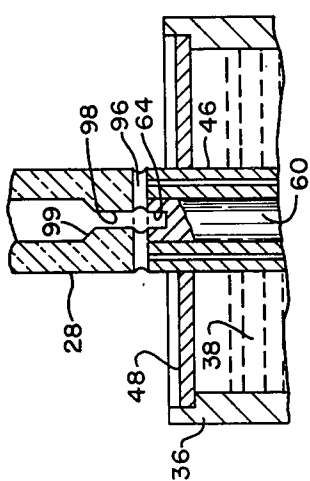


FIG. 5

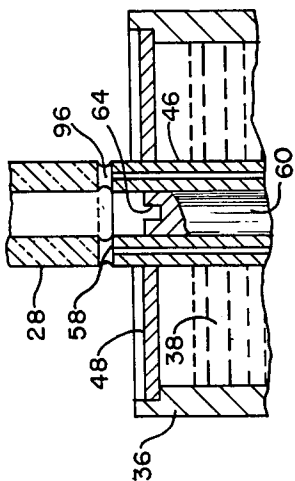


FIG. 4

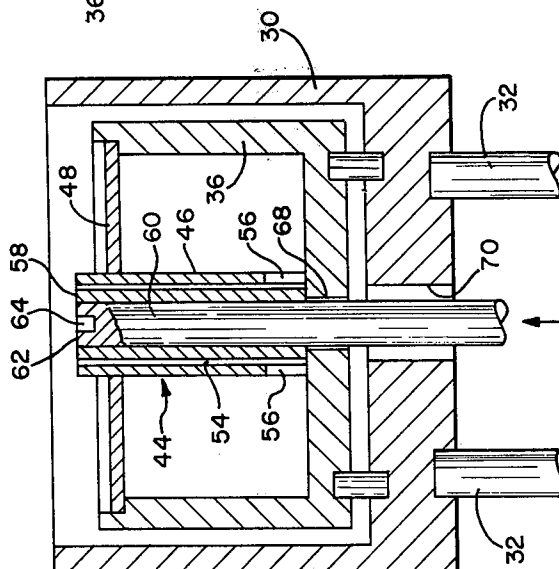


FIG. 2

FIG. 8

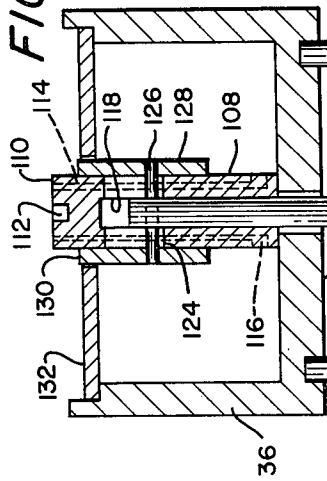


FIG. 6

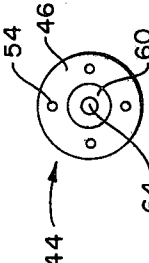
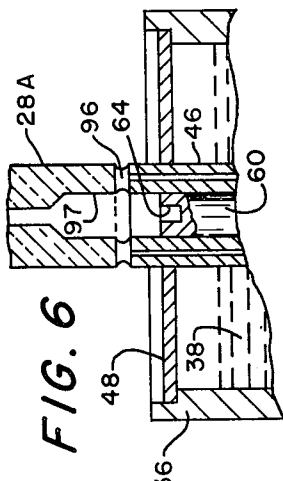


FIG. 7

FIG. 3

APPARATUS FOR GROWING CRYSTALLINE BODIES FROM THE MELT

This application is a division of our copending application, Ser. No. 148,589 filed June 1, 1971 entitled "Method of Growing Crystalline Bodies from the Melt" now abandoned.

This invention relates to monocrystalline tubular bodies and more particularly to production of monocrystalline end walls or flanges on monocrystalline tubes.

Various methods have been developed for growing monocrystalline bodies from a melt. The present invention pertains to an improvement in 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. Pat. application of Harold E. LaBelle, Jr., Ser. No. 700126, filed Jan. 24, 1968 for Method of Growing Crystalline Materials.

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 crystal. 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 of the same shape as the hole desired in the growing body, provided, however, that any such 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 of liquid which is constantly replenished.

The primary object of the present invention is to provide an improved method and apparatus for growing monocrystalline tubes using the EFG technique. An-

other object is to provide new monocrystalline tubular products.

In this connection it is known that the EFG process may be used to grow monocrystalline tubes of selected ceramic materials such as alumina and that tubes made of monocrystalline or polycrystalline alumina have utility as envelopes for high intensity vapor lamps. In the manufacture of such lamps the practice is to mount the electrodes in metal end caps that are attached to the ends of the envelopes by brazing or other suitable technique. It is recognized that mounting of the electrodes may be facilitated by forming the tubes with end walls each having an opening for direct mounting of an electrode without need for an end cap. It is also desirable for other applications to form ceramic tubes each having an imperforate end wall at one end or tubes that are integral extensions of solid rods of the same material or tubes having sections of different internal or external diameters. It also is desirable to form monocrystalline tubes on a continuous basis. Accordingly a more specific object of this invention is to provide an improved method and apparatus for producing monocrystalline tubes of ceramic materials such as alpha-alumina that terminate in integral end walls or flanges.

Another object is to provide a new and improved method of producing tubes of varying cross-sections.

Still another object is to provide a method of growing a monocrystalline body comprising a series of connected tubular sections of like cross-section connected by transition sections whereby the body may be severed at said transition sections to form a plurality of short tubes.

Described briefly, the invention consists of providing a die or forming member comprising a first member having a substantially horizontal end surface adapted to be wet by and used to support a film of melt from which a crystal is to be pulled and one or more vertically extending capillaries that extend down from said end surface, a second member coaxially disposed with respect to said first member and having a correspondingly disposed end surface adapted to be wet by a film of the same melt, and means providing relative movement of said first and second members in an axial direction so as to move said end surfaces into and out of horizontal alignment with each other. A melt of the material to be crystallized is supplied to the lower end of the capillaries and rises to the top ends by capillary action. Then a molten film of melt is formed on the end surface of the first member so as to connect with the melt in the capillaries and a crystal is grown from the film of melt. The film is caused to spread over the entire end surface of the first member and the pulling speed of the crystal and the temperature of the film are controlled so that the crystal grows from the film at all points along its entire horizontal expanse. After the crystal has grown to the desired length, the end surface of the second member is moved into alignment with the end surface of the first member and the film is caused to expand laterally over the entire end surface of the second member. The pulling speed of the crystal and the temperature of the film are controlled so that the crystal now grows from the film overlying both end surfaces. Subsequently the end surface of the second member is moved out of alignment with the end surface of the first member so that crystal growth can occur only from the film overlying the end surface of the first member. Additional melt is continuously supplied by the capillaries to the film on

the first end surface to replace the melt consumed by crystal growth.

Other features and the advantages of the invention are described or rendered obvious by the following detailed description which is to be considered together with the accompanying drawings wherein:

FIG. 1 is an elevational view, partly in section, of apparatus for practicing the method of this invention;

FIG. 2 is an elevational sectional view on an enlarged scale of a portion of the apparatus of FIG. 1;

FIG. 3 is a plane view of a part of the apparatus of FIG. 2;

FIG. 4 is a view similar to FIG. 2 showing one phase of the growth process;

FIGS. 5 and 6 are views similar to FIG. 3 showing other phases of the growth process;

FIG. 7 illustrates one form of tube that can be produced according to the invention; and

FIG. 8 shows apparatus for a modification of the invention.

The present invention may be used to produce monocrystalline tubes 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, notably materials 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 tubes of sapphire, i.e., monocrystalline alumina.

FIG. 1 shows a furnace embodying the invention. The furnace consists of a vertically moveable horizontal bed 2 which engages a stationary furnace enclosure consisting of two concentric-spaced quartz tubes 4 and 6 that are supported at their opposite ends in two annular heads 8 and 10 that seal off the space between the two tubes. The bottom end of the inner tube 4 extends below bottom head 8 and is positioned in a gasket 12 disposed in a cavity in the bed. The bottom head 8 is provided with an inlet port fitted with a pipe 14. The upper head 10 has an outlet port with a pipe 16. Pipes 14 and 16 are connected to a pump (not shown) that continuously circulates cooling water through the space between the two quartz tubes. 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 interior of the furnace enclosure is connected by a pipe 18 mounted in the bed 2 to a vacuum pump or to a regulated source (not shown) of inert gas such as argon or helium. The furnace enclosure also is surrounded by an R.F. heating coil 20 that is coupled to a controllable 500kc. power supply (not shown) of conventional construction. The heating coil may be moved up and down along the length of the furnace enclosure and means (not shown) are provided for supporting the coil at a selected elevation.

The head 10 is attached and supported by a conventional crystal pulling mechanism represented schematically at 22. The crystal pulling mechanism 22 has an elongate pulling rod 24 that extends through the head 10 and into the furnace enclosure. It is to be noted that the type of crystal-pulling mechanism is not critical to the invention and that the construction thereof may be

varied substantially. Preferably, however, we prefer to employ a crystal pulling mechanism that is hydraulically controlled since it offers the advantage 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 22 is adapted to move pulling rod 24 axially at a controlled rate. Pulling rod 24 is disposed coaxially with the quartz tubes 4 and 6 and its lower end has an extension in the form of metal holder 26 that is adapted to releasably hold a seed on which crystal growth is made to occur as hereafter described. By way of example, the seed may be a monocrystalline tube 28 grown previously by the EFG technique.

Located within the furnace enclosure is a cylindrical heat susceptor 30 made of carbon. The top end of susceptor 30 is open but its bottom end is closed off by an end wall. The susceptor is secured to and supported by a plurality of tungsten rods 32 that are anchored in bed 2. Supported within susceptor 30 on a plurality of short tungsten rods 34 is a crucible 36 adapted to contain a melt 38 of the material to be grown in accordance with the invention. Rods 34 are secured to susceptor 30 and crucible 36 so as to prevent movement of the crucible. 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 made of molybdenum but it also may be made of tungsten, iridium or some other material with similar properties with respect to molten alumina. Where a molybdenum crucible is used, it 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 suitable size and shape, preferably with a constant diameter. To help obtain the high operating temperatures necessary for the process, a cylindrical radiation shield 40 made of carbon cloth may be wrapped around the carbon susceptor. The carbon cloth greatly reduces the heat loss from the carbon susceptor.

Referring now to FIGS. 1-3, mounted in crucible 36 is a die assembly identified generally by the numeral 44. The die assembly is made of molybdenum and comprises a cylindrical sleeve 46 that is affixed (e.g. by welding or press fit) to a supporting disc 48 that is locked to the crucible. The bottom end of sleeve 46 is welded to the bottom wall of the crucible so as to prevent leakage of melt to the interior of the sleeve. Sleeve 46 has a plurality of axially extending, circumferentially spaced, circular bores 54 and radial openings 56 near its bottom end to permit inflow of melt to the several bores from the crucible. Bores 54 are sized to function as capillaries for molten alumina. The upper end of sleeve 46 terminates in a flat horizontal surface 58 which intersects the sleeve's outer surface at a right angle. It is to be noted that sleeve 46 projects above disc 48 so as to be visible to the operator. The length of the sleeve 46 and diameter of the capillaries 54 are such that molten alumina can rise in and fully fill the capillaries by action of capillary rise so long as the level of the melt in the crucible is high enough to flow into the openings 56. The height to which a column of melt can rise by capillary action in one of the capillaries 54 can be approximated by the equation $h=2T\cos\theta/drg$, where h is the distance in cm. that the column will rise; T is the surface tension of the melt in dynes/cm.; θ is the contact angle of the melt; d is the density of the melt,

r is the internal radius of the capillary in cm.; and g is the gravitational constant in cm/sec². By way of example in a capillary of 0.75 mm. diameter in a molybdenum member, a column of molten alumina may be expected to rise more than 11 cm. by capillary action.

Slidably disposed with sleeve 46 is a molybdenum rod 60 of circular cross-section. The upper end of rod 60 terminates in a flat horizontal surface 62 having an axially extending cavity 64. The latter has a diameter large enough so that surface tension will not cause a film of melt on surface 62 to fill in over it. In this connection it is to be noted that end surface 62 intersects the outer surface of rod 60 and also the cylindrical surface forming the side wall of cavity 64 at a right angle. Rod 60 is sized so as to make a snug sliding fit with sleeve 46, particularly at the temperature (about 2070°C) at which the die assembly is maintained during crystal growth. Rod 60 extends through a hole 68 in the bottom of the crucible and also through a hole 70 in the bottom wall of susceptor 30. Hole 70 is oversized so as to prevent reaction of the molybdenum rod and carbon susceptor.

Referring now to FIG. 1, the bottom end of rod 60 is connected by a coupling 72 to a larger diameter rod 74 that is slidably mounted in a sleeve bearing 76 that is secured in the bed 2. The lower end of rod 74 is connected by a second coupling 78 to the piston rod 80 of a hydraulic actuator 82. The latter is of the double-acting type, having two inlet ports 84 and 86 at opposite ends of its cylinder. Ports 84 and 86 are connected by hose lines 88 to a suitable source of pressurized hydraulic fluid (not shown) via a suitable reversing valve shown schematically at 90. Valve 90 is adapted to selectively apply fluid under pressure to either of ports 84 and 86. When fluid pressure is applied via inlet port 84, piston rod 80 retracts into the actuator cylinder. Application of fluid pressure to inlet port 86 causes piston rod 80 to be extended. Actuator 82 is mounted on a supporting bracket 92 that is secured to the bed 2. The bed 2 is mounted on a pair of vertical slide rods 94 that are attached to a supporting framework (not shown) that also supports the pulling mechanism. Additionally the bed 2 is supported by a mechanism (not shown) that is adapted to lower and raise the bed and hold it at a selected height. Such bed raising and lowering mechanisms are well known in the art of crystal growing furnaces and, therefore, need not be shown in detail. Preferably, however, the bed raising and lowering mechanism is hydraulically operated.

The apparatus just described is designed to permit growth of tubular crystal bodies that are characterized by spaced internal flanges, i.e., tubes that comprise successive tubular sections of constant inner and outer diameters connected by shorter tubular sections having the same outer but a different inner diameter. For want of a better name, the latter sections may be termed "transition sections." The same apparatus may be used to grow a tube of one wall thickness onto a tube of a different wall thickness. 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 in accordance with the EFG technique described in copending application Ser. No. 700126 of Harold E. LaBelle, Jr. Preferably, however, it is preferred to use a monocrystalline tube previously grown

by the EFG technique. Such tubes are available commercially.

FIGS. 4 and 5 illustrate how a tube having a constant diameter outer surface and a stepped inner surface may be grown according to the invention using the apparatus of FIGS. 1 and 2. It is to be noted that growth may be initiated with rod 60 disposed either in lowered position (FIG. 4) or raised position (FIG. 5). Assuming for purpose of explanation that initially rod 60 is in the lowered position shown in FIG. 4 and the crucible and capillaries are filled with an alumina melt, a previously grown sapphire tube 28 is mounted in holder 26 in axial alignment with the die assembly. Tube 28 has substantially the same o.d. and i.d. as the surface 58. Then with the power input to coil 30 adjusted so that the upper end surface of 58 of sleeve 46 is about 10°–40°C higher than the melting point of the tube 28, the tube is lowered into contact with the surface 58 and held there long enough for a portion of the end of the tube to melt and form a liquid film 96 that connects with the melt in one or more of the capillaries and preferably covers all of the surface 58. It is to be noted that the capillaries are filled with melt but are shown empty in FIGS. 4–6 in order to render the capillaries more distinct to the reader. Further it is to be understood with reference to FIG. 4 that before the end of tube 28 is melted to form film 96, the melt in each capillary has a concave meniscus with the edge of the meniscus being substantially flush with surface 58. The temperature gradient along the length of the tube and the temperature of surface 58 are factors influencing how much of the tube melts and the thickness of the film 96. In this connection it is to be noted that the tube functions as a heat sink so that its temperature is lower at successively higher points thereon. However, the thermal gradient along tube 28 is affected by the height of coil 29 and susceptor 30 and also the power input to the coil. In practice these parameters are adjusted so that the initial film 96 has a thickness in the order of 0.1mm.

Once the film 96 has connected with melt in at least one of the capillaries, the pulling mechanism 34 is actuated to pull tube 28 upwardly away from surface 58. The pulling speed is set so that surface tension will cause the film to adhere to the tube long enough for crystallization to occur due to a drop in temperature at the solid tube-liquid film interface. The drop in temperature occurs because of movement of the tube away from the surface 58, i.e. because the solid-liquid interface sees a lower temperature. If the initial film does not fully cover surface 58, as tube 28 is pulled surface tension will cause the film to spread fully over surface 58 (see FIG. 3). Thus, as tube 28 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 tube which has substantially the same cross-sectional shape and size as the tube. The film consumed by the crystal growth is replaced by additional melt which is supplied by the capillaries 54. The process is continued until the tubular monocrystalline extension has grown to a desired length. Then actuator 82 is operated to raise rod 60 just enough to place its top and surface 62 flush with end surface 58. Once this has occurred, surface tension will cause film 96 to spread radially inward over end surface 62. Adjustment of the pulling speed and/or operating temperature may be required in order to cause the film to spread. In any event, as the film spreads, crystal

growth will also spread until finally it will occur at all points along the horizontal expanse of the film with the result that the newly grown crystal will have substantially the same outer diameter as surface 58 and an inner diameter 98 approximately the same as that of cavity 64 (see FIG. 5). The change in inside diameter of the tube is not sharp but tapered as shown at 99 in FIG. 5. Thereafter the growth may be continued without further change in position of rod 60, in which case the product will comprise a tube having a first section with a relatively large i.d. and a second section with a relatively small i.d., while its o.d. will be substantially constant.

It is also possible to start the growth process with tube 60 retracted but using as a seed a previously grown tube 28A having the same o.d. as sleeve 58 and an i.d. equal to the diameter of cavity 64. In this case the film formed by melting the seed tube will cover only the upper surface 58 of sleeve 46. Accordingly the crystal growth produced on the seed tube as it is being pulled as above described forms a tubular extension having the same o.d. as the original tube, but an i.d. as shown at 97 that is about the same as the i.d. of sleeve 46.

It is contemplated also that rod 60 may be repetitively raised and lowered at selected intervals during the growth process, in which case the product will have alternately occurring sections 100 and 102 of relatively large and relatively small internal diameter (FIG. 7). This product may be cut into shorter lengths at convenient points along either the sections 100 or the sections 102.

In the case of providing envelopes for lamps, it is preferable to cut the product at the transition sections 102. Accordingly the sections 102 are made long enough so that when severed, e.g. along line 104, to form a plurality of discrete tubes, each tube will have an internal flange (which may also be considered as end wall with a center hole) that is thick enough to provide the rigidity required for it to function as a support for a lamp electrode.

It is to be noted that the pulling speed and the temperature of the film may be varied during crystal growth. However, the pulling speed should not be so great and the film temperature so high as to cause the tube to pull free of the melt film. In growing alpha-alumina, it is preferred to have an initial pulling speed of about 0.1 in/min until it is determined that the film fully covers the supporting end surface and to thereafter increase the speed to about 0.2 in/min. The pulling speed and the film temperature control the thickness of the film which also controls the rate at which the film will spread. Within limits, the film thickness can be increased by increasing the film temperature and the pulling speed.

The following example illustrates a preferred mode of practicing the invention.

EXAMPLE I

A molybdenum crucible having an internal diameter of about 1.50 inch, a wall thickness of about 0.20 inch, and an internal depth of about 0.60 in. is positioned in the furnace in the manner shown in FIG. 1. Disposed in the crucible is a die assembly constructed generally as shown in FIG. 2. The sleeve 46 has four capillaries 54 spaced uniformly about its axis. The upper end surface 58 of sleeve 46 has an outside diameter of about

0.500 inch and an inside diameter of about 0.450 inch. The length of sleeve 46 is such that its upper end projects about 1/16 inch above the crucible. The rod 60 has an outside diameter of about 0.445 inch and its cavity 64 has a diameter of about 0.31 inch. The actuator is adapted to move rod 60 through a stroke of about 0.30 inch between upper and lower limit positions. In the upper limit position, its upper end surface 62 is flush with end surface 58. The four capillaries each have a diameter of about 0.03 inch. The crucible is filled with substantially pure polycrystalline alpha-alumina and a monocrystalline alpha-alumina tube 28 grown previously by the EFG technique is mounted in holder 26. Tube 28 is cylindrical and was grown so that the c-axis of its crystal lattice extends parallel to its geometric axis. Additionally, tube 28 has substantially the same inside and outside diameter as surface 58 of sleeve 46. Tube 28 is mounted in holder 26 so that it is aligned with surface 58. Access to seed holder 26 and the crucible 36 is achieved by lowering bed 2 away from the furnace enclosure and lowering the seed holder below the bottom end of furnace tube 4. With the bed restored to the position of FIG. 1, rod 60 is lowered to its lower limit position (FIG. 4). Cooling water is introduced between quartz tubes 4 and 6 and 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 R.F. coil 20 is energized and operated so that alumina in the crucible is brought to a molten condition (alumina has a melting point in the vicinity of 2050°C) and the surface 68 reaches a temperature of about 2070°C. As the solid alumina is converted to the melt 38, columns of the melt will rise in and fill capillaries 54. Each column of melt will rise until its meniscus is substantially flush with the top of the rod. After affording time for temperature equilibrium to be established, the pulling mechanism is actuated and operated so that the tube 28 is moved into contact with the upper surface 58 of the die assembly and allowed to rest in that position long enough to allow the bottom end of the tube to melt and form film 96. After about 60 seconds, the tube is withdrawn vertically at the rate of about 0.1 inch per minute. As the tube is withdrawn, crystal growth will occur on the seed and at the same time, if it does not already fully cover surface 58, the film 96 will spread fully over the surface 68 due to its affinity with the newly grown material on the tube and the film's surface tension. The latter force also causes additional melt to flow out of the capillaries and add to the total volume of film.

As the tube 28 is pulled, the crystal growth will propagate vertically throughout the entire horizontal expanse of the film 96, with the result that growing crystal will conform in cross-sectional shape to the surface 58. At this point the pulling speed is increased to about 0.2 inch/min. and the temperature of the surface 58 held constant at about 2070°C. Growth is continued until a monocrystalline tubular extension of about 4 inches has been produced on the seed tube. Then, as pulling continues, actuator 82 is operated to raise rod 60 to its upper limit position (FIG. 5) so as to place its surface 62 even with surface 58. Once this has been done, the film 96 will begin to spread onto surface 62. Spreading of the film is helped by raising the temperature of surface 58 to about 2080°C. As the film begins to spread radially inward over surface 62, the crystal growth will also expand horizontally. The film stops spreading

when it reaches the edge of cavity 64, and as pulling continues the crystal growth will propagate vertically throughout the entire horizontal expanse of the expanded film, with the result that the growing crystal will now have the same o.d. as sleeve 46, but an i.d. as shown at 98 (FIG. 5). Crystal growth is continued until that portion of the tubular extension having the reduced diameter 98 reaches a length of $\frac{1}{2}$ inch, whereupon the pulling speed is increased to about 1.0 inch per minute. At this higher pulling speed, the crystal body pulls free of the melt film. Thereafter, the pulling mechanism is stopped and the furnace cooled. The tube 28 is retrieved from holder 26. The grown body is found to be substantially monocrystalline and a crystallographic extension of the crystal lattice of the seed tube 28. Its outside diameter is substantially constant and approximately the same as the o.d. of sleeve 46. Its inner surface comprises a long section (about 4 inches) with a diameter about the same as the i.d. of sleeve 46, and two shorter sections, one having a diameter of about the same as cavity 64 and the other being tapered as shown at 99. The inner and outer surfaces are both smooth.

EXAMPLE II

In this example, the seed tube and the procedure are the same as in Example I, except that growth is not terminated after that portion of the tubular extension having the reduced diameter 98 has reached a length of about $\frac{1}{2}$ inch. Instead that portion is allowed to grow to a length of about $\frac{3}{4}$ inch, whereupon rod 60 is lowered to its original position (FIG. 4). Rod 60 is lowered at a rate such that as it drops the surface tension will cause film 96 to recede radially away from cavity 64 until surface 62 is substantially completely free of melt film. Rod 60 preferably is lowered at a rate in the order of the pulling speed of tube 28. As the film recedes from surface 62, the crystal growth also decreases horizontally while continuing to propagate vertically from the film, with the result that the growing body has a gradually expanding internal diameter. Once the film has returned to the internal edge of surface 58, it stops shrinking and now the crystal body continues to grow vertically with substantially the same o.d. and i.d. as sleeve 46. The crystal is allowed to grow an additional 4 inches and then rod 60 is again elevated to the position shown in FIG. 5, whereupon the film again expands over the surface 62 and the crystal again grows to the diameter of cavity 64. Thereafter rod 60 is repeatedly lowered and raised to repeatedly vary the internal diameter of the product as above described. The result is a product having a stepped internal wall as shown in FIG. 7.

Although a monocrystalline tube has been used as the seed to initiate crystal growth, it also is possible to start with a seed of some other shape, e.g. a monocrystalline ribbon or filament, and grow a tube therefrom as described in the aforesaid copending application of Harold E. LaBelle, Jr. Once the body has reached a tubular shape, it may be grown so as to have a stepped internal surface as herein described.

It is to be noted that the invention may be used in growing tubular or rod extensions (or flanges or end walls) of other cross-sectional shapes, e.g. rectangular, square, triangular, etc. on tubes or rods of the same or different cross-sections. Thus, for example, by making the cross-section of rod 60 and cavity 64 and the inner

edge configuration of sleeve 46 square, it is possible to grow a tubular extension or termination of square interior shape and round exterior shape onto a tube of round or square cross-section. By eliminating cavity 64 and positioning rod 60 as in FIG. 5, it is possible to grow a solid rod onto a tube. Also, by way of example, by making cavity 64 triangular or hexagonal and the outer edge configuration of sleeve 46 square, it is possible to grow a tubular extension with a cross-sectional configuration that is triangular or hexagonal on the interior and square on the exterior.

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 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. Additionally, certain minor changes may be required in the apparatus, e.g., different crucible materials in order to avoid reaction between the melt and the crucible.

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. Therefore, for convenience and in the interest of avoiding any suggestion that the crystal growth is polycrystalline in character, we prefer to describe it as "substantially monocrystalline," it being understood 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.

It also has been found that best results are achieved if the c-axis of the crystal lattice of the seed tube extends parallel to the tube's longitudinal axis, so that the extension forming a flange or end wall also grows vertically along the c-axis. Growth in the c-direction is characterized by smooth surfaces and superior strength.

Obviously the invention is susceptible of modification and may be practiced otherwise than as specifically described above. For example, it is possible to grow tubular rods having a varying external cross-sectional configuration, e.g., a tube having spaced external flanges rather than internal flanges. This may be accomplished by using a die assembly having a close fitting sleeve slidably disposed around the outside of a stationary die member having one or more capillaries, and means for raising and lowering the sleeve in the same manner as rod 60. FIG. 8 illustrates one possible die arrangement for growing tubular bodies with varying external cross-sectional configurations. In this case the die assembly consists of a cylindrical rod 108 having a flat top end surface 110 with a cavity 112 (which serves the same purpose as cavity 64) and a plurality of capillaries in the form of through bores 114. The bottom end of rod 108 has side openings 116 to admit melt to the capillaries. Rod 108 also has a large center bore

118 in which is slidably disposed a slide rod 120 that extends through a hole in the bottom wall 122 of crucible 36. Although not shown, it is to be understood that the bottom end of slide rod 120 is connected to operating rod 72 so that it may be raised or lowered by actuator 82. Rod 108 also has two diametrically opposed slots 124 in that portion thereof that defines bore 118. Slots 124 are wide enough to slidably accommodate portions of a pin 126 that is carried by slide rod 120. The ends of pin 126 are anchored in a cylindrical sleeve 128 that surrounds and makes a close sliding fit with the rod 108. The upper end of sleeve 128 has a flat annular surface 130. The upper end of the crucible is covered by a removeable disc 132 that functions as a radiation shield for the melt and has a center hole to slidably accommodate sleeve 128. It is to be understood that actuator 82 can move sleeve 128 from a suitably lower limit position such as shown in FIG. 8 to an upper limit position in which its annular end surface 130 is flush with the upper annular end surface 110. When sleeve 128 is in its lower limit position, crystal growth occurs from a film of melt supported by the end surface 110. When sleeve 128 is in its upper limit position, the film of melt can be made to cover its end surface 130 as well as surface 110 and crystal growth occurs from this larger film of melt. In other words, when sleeve 128 is down, the crystal growth will conform in cross-sectional configuration to the annular shape of surface 110, whereas when sleeve 128 is raised, the crystal growth will have an exterior diameter close to the diameter of cavity 112. Leakage of melt via the hole provided in the bottom of the crucible for rod 120 is avoided by welding the bottom end of rod 108 to the crucible's bottom wall. Initial formation of a film of melt on the upper end surface 110 of the capillary assembly may be achieved in a manner similar to that described above in connection with Example I, but preferably using as a seed a previously grown monocrystalline tube having an o.d. no greater than the o.d. of end surface 110. If the melt and seed tube are alumina, the operating temperature and pulling speed are the same as in Example I and outward expansion of the melt film onto surface 130 is conducted by controlling the operating temperature and pulling speed in the same manner as employed in Example I to achieve inward expansion from surface 58 onto surface 62. The apparatus of FIG. 8 may be used to grow a tubular or solid rod extension (or an exterior flange) of a relatively large outside diameter on a tube or rod of relatively small outside diameter and as with the die assembly of FIG. 2, the die assembly of FIG. 8 may be modified so as to grow bodies of round, square, rectangular or other like cross-sectional configurations. In this connection it is to be noted that a solid rod may be grown by omitting cavity 112.

With respect to the die assembly, it is to be understood that in the following claims the term "surface" as it pertains to a die member is intended to cover the effective film-supporting surface of that die member, whether the member is made as a single piece or as two or more pieces, and the term "capillary" is intended to denote a passageway that can take a variety of forms. In this connection it is to be noted that the sleeve 46 of FIG. 2 may actually consist of two concentric spaced sleeves locked against relative movement and spaced uniformly so as to provide a continuous annular space therebetween that is adapted to function as one large capillary. Thus, in the die assembly of FIG. 2, sleeve 46

may be replaced by two round sleeves locked to each other in concentric spaced relation, with the annular space therebetween measuring about 0.03 inch in a radial direction. Of course, since the annular space functions as a capillary, the two sleeves need not have bores like those shown at 54, but the outer sleeve must have openings at its bottom end (corresponding to openings 54) to permit inflow of melt to the annular capillary. The rod 60 would be disposed within the inner one of the concentric sleeves. The effective film supporting surface of a die member having one or more capillaries is understood to be its entire end surface considered as if the capillary orifices were not present since when a film of melt fully overlies the end surface it covers over the capillary orifices.

What is claimed is:

1. Apparatus comprising a crucible, a die assembly extending into said crucible having first and second concentric members each having a substantially horizontal top end surface, said first member having at least one passageway that terminates at one end in an orifice in the said top end surface of said first member and communicates at the opposite end with the interior of said crucible, said members being mounted for relative axial movement so that the said top end surface of one member can be moved into and out of horizontal alignment with the said top end surface of the other member.

2. Apparatus according to claim 1 wherein one of said members is stationary and the other of said members is moveable axially.

3. Apparatus according to claim 1 further including means for causing relative axial movement of said members.

4. Apparatus according to claim 1 wherein said first member surrounds said second member.

5. Apparatus according to claim 4 wherein said first member is locked to said crucible and said second member is mounted for axial movement relative to said crucible and said first member.

6. Apparatus according to claim 5 wherein said second member projects out of the bottom of said crucible, and further including means for moving said second member.

7. Apparatus according to claim 4 wherein the said end surface of said first member is annular.

8. Apparatus according to claim 7 wherein said end surface of said second member is annular.

9. Apparatus according to claim 1 wherein at least part of said die assembly is supported by said crucible.

10. Apparatus according to claim 1 wherein said second member surrounds said first member.

11. Apparatus comprising a die assembly having first and second members each having a substantially horizontal surface at a corresponding end thereof, at least one passageway in one of said members that communicates at one point with an orifice in the said surface of said one member and has an inlet at a point below said orifice, means for supporting said die assembly, means for holding a supply of melt in communication with said inlet, and means for moving one of said members relative to the other so as to move said surfaces into and out of horizontal alignment with each other.

12. Apparatus according to claim 11 further including means for heating said die assembly.

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