Nov. 5, 1974 H. E. LABELLE. JR., ET AL 3,846,082

PROUCTION OF CRYSTALLINE BODIES OF COMPLEX GEOMETRIES

Filed Nov. 8, 1971 3 Sheets-Sheet 1

FIG. 1

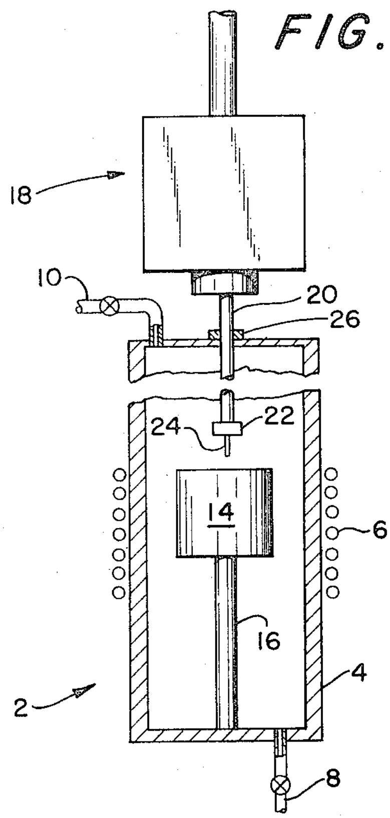
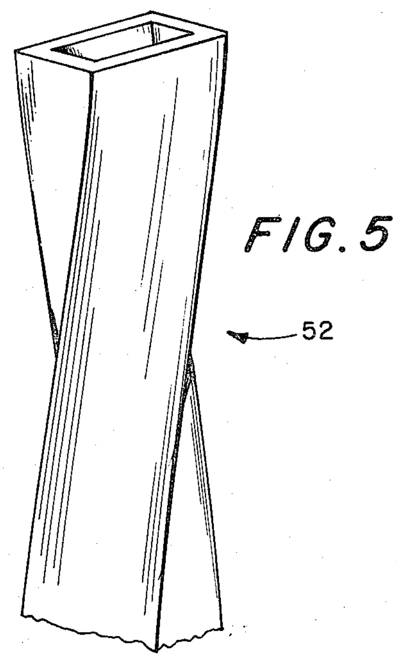


FIG. 5



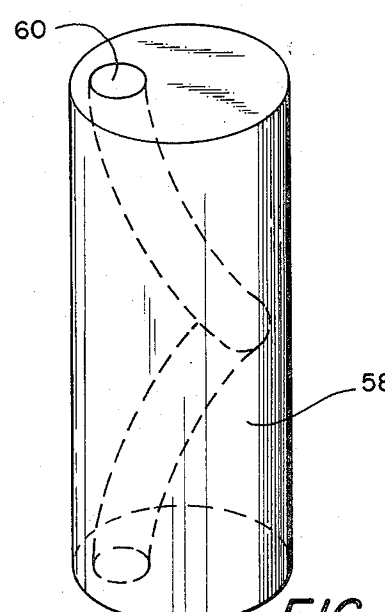


FIG. 8

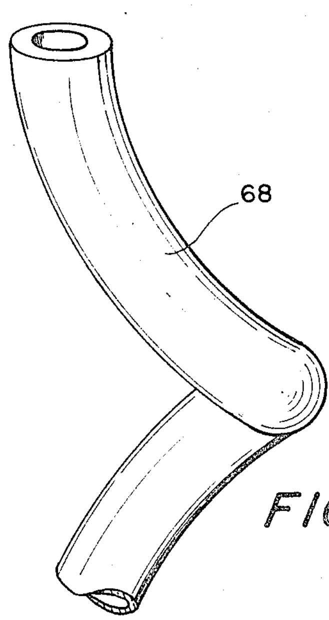


FIG. 10

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PROUCTION OF CRYSTALLINE BODIES OF COMPLEX GEOMETRIES

Filed Nov. 8, 1971 3 Sheets-Sheet 2

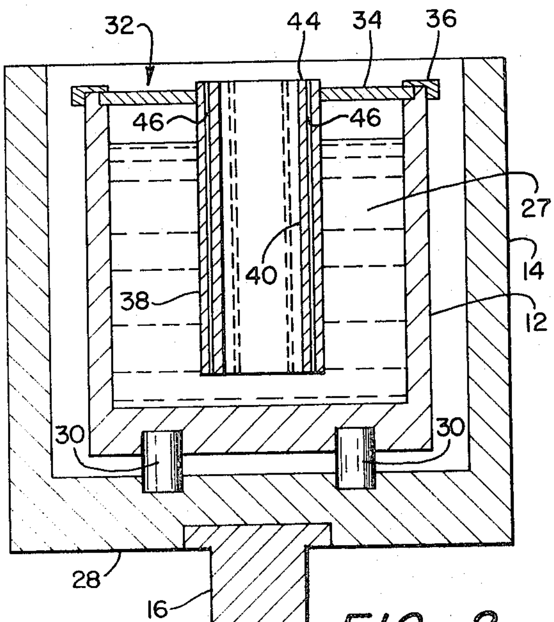

FIG. 2

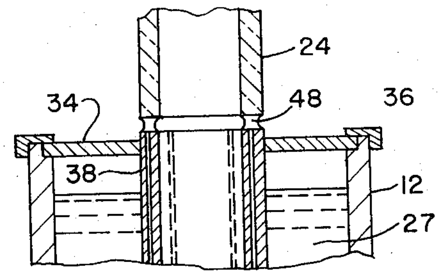

FIG. 4

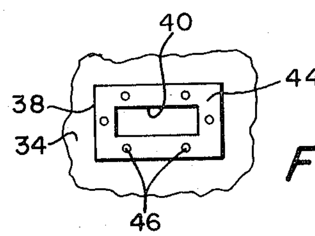

FIG. 3

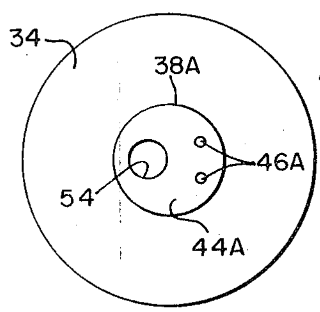

FIG. 7

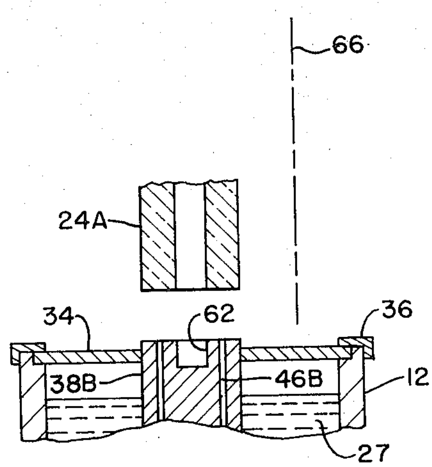

FIG. 9

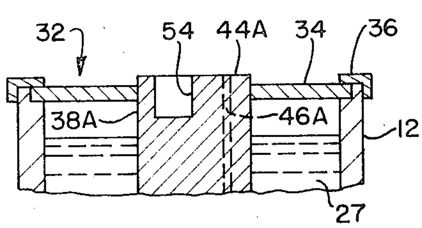

FIG. 6

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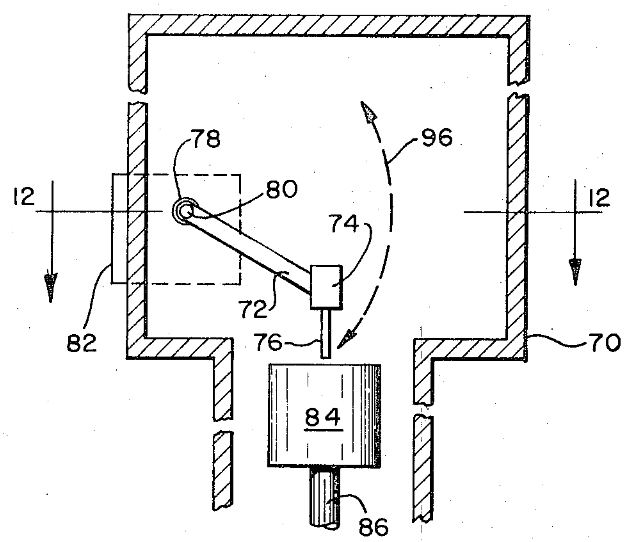

FIG. 11

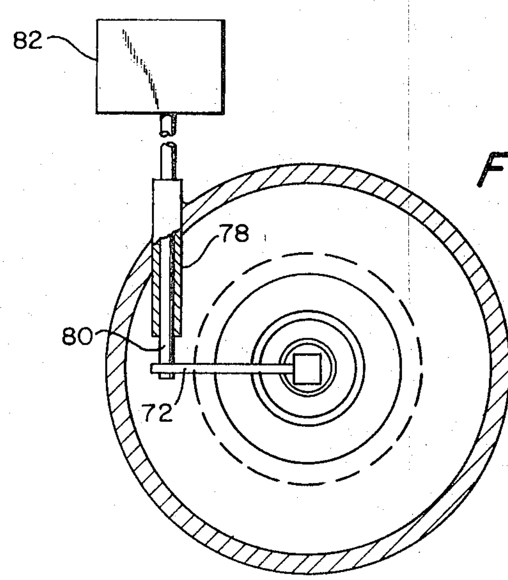

FIG. 12

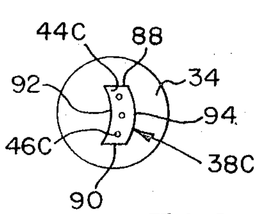

FIG. 13

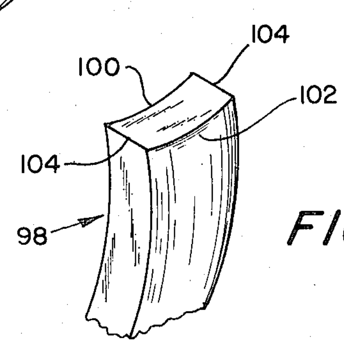

FIG. 14

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PRODUCTION OF CRYSTALLINE BODIES OF COMPLEX GEOMETRIES

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Int. Cl. B01j *17/00*

U.S. Cl. 23—301 SP 13 Claims

ABSTRACT OF THE DISCLOSURE

The invention provides a method of growing monocrystalline bodies of various complex shapes from a liquid film of predetermined edge configuration. The invention is based on the EFG process disclosed in U.S. Pat. No. 3,591,348 and essentially comprises rotating the growing crystal body about a selected axis as it is being pulled from the liquid film, whereby the shape of the crystal body is a function of its rotational mode and the configuration of the liquid film.

This invention relates to production of essentially monocrystalline bodies with outside and/or inside surfaces of complex geometries.

The present invention involves the so-called EFG process previously known for growing monocrystalline bodies of materials such as alumina. The term "EFG" stands for "edge-defined, film-fed growth" and designates a process for growing crystalline bodies from a melt. The essential features of the EFG process are described in U.S. Pat. No. 3,591,348, issued July 6, 1971 to Harold E. LaBelle, Jr. 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 a horizontal 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 crystalline bodies with a variety of 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 reservoir of melt 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. Thus it is possible to grow a substantially monocrystalline body with any one of a variety of predetermined cross-sectional configurations, e.g. bodies with circular, square or rectangular cross-sections. Furthermore, since the liquid film has no way of discriminating between an outside or inside edge of the die's end surface, it is possible to grow a monocrystalline body with a continuous hole by providing in that end surface a blind hole, i.e. a cavity of the same shape as the hole desired in the growing body, provided, however, that any such blind hole is made large enough so that surface tension will not cause melt film around

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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.

It has been determined that essential factors contributing to the essentially monocrystalline character of the bodies that are grown by the EFG process are the fact that the film-supporting surface of the die functions as a substantially iso-thermal heater (i.e. the film-supporting surface has a substantially flat temperature profile along its entire expanse), and the fact that the melt film is not affected by perturbations in the melt reservoir and can be maintained at an average temperature different than the average temperature of the melt in the reservoir.

The present invention is a modification of the EFG technique and has as its primary object the production directly from the melt of crystalline bodies characterized by complex shapes.

A further object of this invention is to provide a new method based on the EFG process of producing crystalline bodies of various complex shapes.

A more specific object of the invention is to produce new and unique essentially monocrystalline bodies of selected materials, including bodies having an axial twist.

Other specific objects of this invention are to produce essentially monocrystalline bodies in the shape, for example, of a round rod with a spiral hole extending along its length, a hollow tube of polygonal interior and exterior edge configuration characterized by a twist around its growth axis, a helical rod or tube, or a plate of dual axis curvature.

Essentially the invention whereby the following objects are achieved comprises growing a crystalline body from a thin film of melt established and maintained according to the EFG technique and rotating the growing crystal body about a selected axis at a controlled rate so that successive accretions of crystal growth form a body having a predetermined cross-sectional configuration coupled with a predetermined lengthwise configuration. The growing body may be rotated, for example, about an axis that is (a) coincident with the pulling axis; (b) not coincident but parallel to the pulling axis; or (c) transverse to the direction of crystal growth. Other features of the present invention are described in or rendered obvious by the following detailed specification which is to be considered together with the accompanying drawings wherein:

FIG. 1 is a vertical view, partly in section, of a furnace apparatus employed in practicing the invention;

FIG. 2 is a vertical view, partly in section and on an enlarged scale, of a crucible, die and heat susceptor assembly employed in the apparatus of FIG. 1 for growing a twisted hollow tube of rectangular cross-section;

FIG. 3 is a plan view of a portion of the apparatus of FIG. 2;

FIG. 4 is a fragmentary view of the apparatus of FIG. 2 illustrating the initial stage of growth of a twisted hollow tube of rectangular cross-section;

FIG. 5 illustrates the body grown with the apparatus of FIGS. 2 and 3;

FIG. 6 is a fragmentary view similar to FIG. 2 of a crucible and die assembly for growing a rod of circular cross-section with a spiral circular hole extending along its length;

FIG. 7 is a plan view of the die assembly of FIG. 6;

FIG. 8 illustrates the body grown with the apparatus of FIGS. 6 and 7;

FIG. 9 is a view similar to FIG. 6 of a crucible and die assembly for growing a helical hollow tube of circular cross-section;

FIG. 10 illustrates the body grown with the apparatus of FIG. 9;

FIG. 11 is a fragmentary sectional view of apparatus for growing a plate of dual axis curvature;

FIG. 12 is a cross-sectional view taken along line 12—12 of FIG. 11;

FIG. 13 is a plan view of the die assembly employed to grow a plate of dual axis curvature; and

FIG. 14 illustrates on an enlarged scale the shape of the body grown with the apparatus of FIGS. 11–13.

Corresponding parts in the several figures are identified by the same numerals.

It has been discovered that because of the nature of the EFG process (whereby bodies can be grown to predetermined and arbitrary cross-sectional configurations, e.g. circular or rectangular tubes, rectangular plates, etc.), it is possible by rotating the growing body at a selected angular velocity related to the rate of crystal growth, to produce essentially monocrystalline bodies that are characterized by lengthwise curvature of an interior or exterior surface. It is recognized that rotation of a crystalline body, or a crucible from which a crystalline body is pulled, is old. Thus, U.S. Pat. No. 3,552,731 discloses that it is old to employ rotation in practicing the so-called Vernciul method, the Bridgman-Stockbarger technique, and the floating zone technique. However, heretofore rotation has been utilized to facilitate uniform crystal growth and, at least insofar as it is used in the aforementioned prior art processes, rotation does not have the effect of perceptibly modifying the shape of the growing crystal body.

Referring now to FIG. 1, there is shown a furnace **2** comprising a housing **4** and heating means in the form of an RF coil **6** which is coupled to a controllable RF power supply (not shown). The coil may be moved up or down along the length of the housing and means (not shown) are provided for supporting it in any selected elevation. The housing **4** has a pair of valve-controlled lines **8** and **10** for introducing and withdrawing any gas which may be required to control the atmosphere within it. The housing is fluid-tight and, although not shown, it is to be understood that the housing is so constructed as to permit access to its interior for the purpose of introducing a charge of feed material and attaching a seed to the pulling mechanism hereinafter described. The charge of feed material is contained within a crucible **12** (see FIG. 2) that is surrounded by a heat susceptor **14** and is held at a desired position by means of a supporting member **16** that is affixed to the bottom of the housing. Associated with the furnace is a pulling mechanism **18** that includes a pulling rod **20** provided with a chuck **22** for supporting a seed crystal **24**. The pulling rod **20** passes through a suitable seal **26** so that the main portion of the pulling head can be located outside of the furnace as shown. Although not shown in detail, it is to be understood that the pulling mechanism is designed to impart both rotational and reciprocal translational movement to the pulling rod **20**. Such pulling mechanisms are well known in the art of crystal growth and hence their constructions form no part of the present invention. The specific form of the pulling mechanism is not critical to the invention provided it is capable of providing the desired rotational and translational movement. Preferably the pulling mechanism is constructed as described and illustrated in U.S. Pat. No. 3,552,931, issued Jan. 5, 1971 to Paul R. Doherty et al. for "Apparatus for Imparting Translational and Rotational Motion." The pulling mechanism of Doherty et al. employs separately controllable drive means for achieving rotational and translational movement.

Referring now to FIG. 2, the heat susceptor **14** is cylindrical and has a bottom wall **28** that is affixed to the supporting member **16**. The top end of the susceptor is open in order to allow insertion of crucible **12** which is supported in spaced concentric relation to the susceptor by a plurality of pins **30**. The crucible is made of a material

that will not react with or dissolve in the melt, i.e., the molten charge of feed material. Mounted within crucible **12** is a die assembly identified generally by the numeral **32** and comprising a disc **34** that is secured to the crucible by a ring **36** and a rod **38** that is secured to and supported by disc **34**. Disc **34** also functions as a heat shield and cover for the crucible. Rod **38** is made of a material that is wetted by the molten charge of feed material. Rod **38** is of rectangular cross-section and is formed with a rectangular bore **40** which is large enough in cross-sectional area so that it will not function as a capillary for the molten charge of feed material which is represented at **27**. In this connection it is to be noted that the bore **40** need not extend for the full length of the rod but may terminate short of its bottom end so as to form a blind hole or cavity extending down from the upper end surface **44**. The latter is flat, extends substantially horizontally, and terminates in sharp inside and outside edges as shown. Rod **38** terminates close to but short of the bottom of the crucible and is provided with a plurality of small capillaries **46** that extend lengthwise of its wall and terminate in the rod's upper and lower end surfaces. The capillaries are sized so that by capillary action a column of melt will rise in and fill them up to the top surface **44** so long as the bottom ends of the capillaries are submerged in the melt within the crucible. It is to be noted that the height to which a column of a molten material can rise in a capillary is determined by the equation

$$h=2T\cos\phi/drg$$

where h is the distance in cm. that the column will rise above the level of the melt in the crucible; T is the surface tension in dynes/cm.; ϕ is the contact angle; d is the density of the liquid; r is the internal radius of the capillary in cm.; and g is the gravitational constant in cm./sec.^{2}. By way of example, in a capillary of about 0.75 mm. diameter in a molybdenum member corresponding to rod 38, a column of molten alumina may be expected to rise more than about 11 cm. above the level of the melt in the crucible as a result of capillary action.

The manner in which a substantially monocrystalline tube of a ceramic material characterized by a rectangular cross-section and an axial twist is produced using the apparatus of FIGS. 1–3 will now be described. First a seed crystal **24** (of the same composition as the feed material) is mounted in chuck **22** with the pulling rod **20** axially aligned with rod **38** of the die assembly. Then with the crucible filled with an inert gas, the RF coil **6** is energized to melt the charge. The capillaries fill with melt by action of capillary rise from the pool of melt **27** in the crucible and the power input to the RF coil is adjusted so that the upper surface **44** of the die is about 10–40° C. higher than the melting point of the seed crystal. The column of melt in each capillary has a concave meniscus with the edge of the meniscus being substantially flush with surface **44**. It is to be noted that the seed crystal may be in any suitable shape, e.g. a round or rectangular rod or tube. Preferably it has been grown previously by the EFG technique so that its cross-sectional shape corresponds to the configuration of surface **44**, as shown in FIG. 4. Next the seed crystal is lowered into contact with the surface **44** and held there long enough for a portion of the seed to melt and form a liquid film **48** that overlies surface **44** and connects with the melt in the capillaries. The temperature gradient along the length of the seed and the temperature of surface **44** are factors influencing how much of the tube melts and the thickness of film **48**. In this connection it is to be noted that the tube functions as a heat sink and the temperature of the tube at successively higher points thereon is affected by the height of coil **6** and susceptor **14** and also the power input to the coil. In practice these parameters are adjusted so that the initial film **48** has a thickness in the order of 0.1 mm.

Once the film **48** has connected with melt in the capillaries, the pulling mechanism **18** is actuated so as to pull seed **24** upwardly away from surface **44** without any rotation. The pulling speed is set so that the film adhering to the tube because of surface tension will crystallize due to a drop in temperature at the solid tube liquid-film interface which occurs as a result of the pulling (it is to be noted that this interface is substantially planar and parallel to surface **44**). The pulling speed also must be such that surface tension will cause the film to spread fully over the surface **44** (but only if the film initially formed covers less than all of the surface). As the seed is withdrawn, 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, the extension being characterized by a rectangular inside and outside configuration in cross-section. The film consumed by the crystal growth is replaced by additional melt which is supplied by the capillaries **46**. Once the film **48** fully covers the surface **44** and growth is occurring from all points along the film, the pulling mechanism is caused to rotate the pulling rod at a selected accurately controlled angular velocity without interrupting its upward movement. The seed crystal rotates with the pulling rod and as this occurs, the crystal growth continues. The successive accretions of solid continue to produce a tubular extension; however, because of the relative rotation of the seed with respect to the surface **44** and the adherence of film to the growing body due to surface tension, successive accretions are angularly displaced about the pulling axis in accordance with the rate of rotation of the pulling rod. Growth is continued until the supply of melt is exhausted to the point where it is insufficient to maintain the film **48** or until the body has reached a desired length. In the latter case growth is terminated by increasing the pulling speed to a level at which the crystal body pulls free of the melt film.

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 nor the temperature so high as to cause the tube to pull free of the melt film. In growing an alpha-alumina tube, for example, it is preferred to have an initial axial pulling speed of about 0.1 inch per minute and to increase the speed to about 0.2 inch per minute after the film has expanded enough to fully cover the end surface of the die assembly heated as above described. The pulling speed of the tube and the temperature of the film control the film thickness which controls the rate of film spreading. Increasing the temperature of surface **44** (and hence the temperature of the film) and increasing the pulling speed each have the effect of increasing the film thickness.

FIG. 5 illustrates the shape of an essentially monocrystalline body **52** grown with the apparatus of FIGS. 2 and 3 as above described. The body is a hollow tube whose cross-section is characterized by rectangular inner and outer edge configurations and corresponds in shape and size to that of the surface **44** (the openings of capillaries **46** are ignored since the film **48** extends over them). The inner and outer surfaces of body **52** are smooth but are curved as shown because the body has an axial twist, i.e., has a rotational transformation, resulting from rotation of the pulling rod during the growth process.

Essentially growth proceeds by successive monomolecular layer accretions and an essential requirement for achieving the desired rotational transformation of the growing crystal is the constancy of the film **48**. The film thickness is relatively small (typically in the order of about 0.1 mm.) compared to the rate of growth of the growing crystal and the axial movement of the pulling rod. Thus with a film thickness of about 0.1 mm., about 10 volumes of film (disregarding any solid-liquid density difference) are required for the body to grow about 1 cm. Notwithstanding this turnover requirement, the film thickness remains substantially constant due to continual inflow of fresh melt via the capillaries.

In order for rotational transformation of the growing body to occur as above described, the angular velocity of the body about the pulling axis must not be so great as to produce a shearing action in the film or overcome the surface tension forces which cause the film to wet and adhere to the growing solid at the interface therewith. Assuming that this requirement is met, at any given instant in the growth process growth is occurring on the crystal body from all points along the full expanse of the film and the crystal body undergoes rotational transformation with successive monomolecular accretions of solid.

FIGS. 6 and 7 show a crucible and die assembly which may be used to grow a rod having a longitudinally and spirally extending hole. This same apparatus may be used to grow a straight hollow tube according to the conventional EFG technique. In this case, the die assembly **32** comprises a circular rod **38A** having a circular cavity **54** in its top end surface **44A** and a plurality of capillary-sized, longitudinally-extending bores **46A**. The crucible and die apparatus of FIG. 6 is mounted in the furnace housing within susceptor **14** so that the axis of rod **38A** is aligned with the axis of pulling rod **20**. With a seed crystal mounted in chuck **22**, a film is established on surface **44A**, and crystal growth is produced according to essentially the same procedure as described above in growing the rectangular tube of FIG. 5. With the film surrounding cavity **54** and growth occurring from all points along the full horizontal expanse of the film, the growing body will have a circular cross section characterized by a hole conforming in size to cavity **54**. As the growing body is rotated, successive accretions will have the same cross section except the hole produced because of absence of melt film at the location of cavity **54** will be displaced angularly about the growth axis. The resulting crystal body is illustrated in FIG. 8. Essentially it is a straight rod **58** with a cylindrical outer surface characterized by a longitudinally extending bore **60** that curves in a helix coaxial with the rod's center axis.

FIG. 9 illustrates a die apparatus which is like that of FIG. 6 except that its rod **38B** has a circular cavity **62** that is centered with respect to its film-supporting surface **44B**. Melt is supplied to surface **44B** by a plurality of capillaries **46B**. This crucible and die apparatus is mounted in the furnace so that rod **38B** is displaced laterally, i.e., eccentric, with respect to pulling rod **20**. However, the seed is mounted in chuck **22** so that its bottom end is aligned with rod **38B**. This may be accomplished by mounting the seed in the chuck in eccentric relation to the axis of pulling rod **20**. With this arrangement, crystal growth conducted in the manner described above, but with the seed **24A** and growing crystal rotating around an axis (represented by the broken line **66** in FIG. 9) that is displaced from the axis of rod **38B**, will result in a body having the shape shown in FIG. 10. Essentially, the body **68** of FIG. 10 is a hollow tube of elliptical cross-section arranged in the form of a helix.

Of course it is also possible with the apparatus of FIG. 6 to rotate the growing body about an axis eccentric to the axis of rod **38A**. If this is done, the grown body will be a hollow helix the same as that shown in FIG. 10, except that the through bore will not be coaxial, i.e., a cross-section of the hollow helix will have essentially the same shape as the rod of FIG. 8.

FIGS. 11–14 relate to an extension of the discovery that compound movement of the pulling rod with respect to an EFG die can result in essentially monocrystalline bodies of unique shape. In this case the crystal growing furnace comprises a housing **70** modified to provide support for an arm **72** carrying at one end a chuck **74** for holding a seed crystal **76**. The support for arm **72** comprises a sleeve **78** which extends through and is mounted to the wall of the furnace housing and a shaft **80** which is rotatably mounted in sleeve 78. Arm 74 is affixed to the inner end of shaft 80. The opposite end of shaft 80 is connected to a reversible electric motor 82 which is rigidly supported by suitable support means (not shown). Shaft 80 extends horizontally and is displaced laterally from the center axis of the susceptor-crucible-die assembly 84 which is supported on rod 86 affixed to the base of the housing. The assembly 84 comprises a die which, as seen in plan view in FIG. 13, comprises a disc 34 supporting a vertically extending rod 38C that has four longitudinal surfaces, one pair of which (see 88 and 90) are straight and parallel and the other pair of which (see 92 and 94) are also parallel, but with one concave and the other convex. Rod 38C also has a plurality of capillaries 46C that open into its top end surface 44C. The assembly 84 is disposed in the furnace so that the rod 38C is aligned with seed 76 when the arm 72 is lowered to a selected position as shown in FIG. 11. Assuming that a film of melt is established on surface 44C in the manner described above, arm 72 is raised by operation of motor 82 under thermal condition conducive to crystal growth thereon. The growing crystal body will grow to a cross-section corresponding to the configuration of surface 44C. Additionally, because of the fact that rotation of arm 72 will cause the seed to rotate through an arc, as indicated by the broken curved line 96 in FIG. 11, successive accretions of grown crystal will form an extension that is curved according to the arc of movement of the seed crystal. FIG. 14 shows the shape of the resulting crystal body 98. As illustrated, its cross-section has relatively broad concave and convex sides 100 and 102 that correspond in size and shape to the side edges 92 and 94 and extend between two straight parallel sides 104 that correspond in size and shape to side edges 88 and 90. Additionally, the body is curved lengthwise. Thus, the body corresponds to a section of a sphere.

Even more complex shapes can be produced. Thus it is possible to combine rotation of the seed crystal with the pulling movement of the apparatus of FIGS. 11–13, with the result that the crystal body will be like that of FIG. 14 except that it also will have a helical transformation along the direction of growth. Another possible variation is to reverse rotation of the seed one or more times or intermittently rotate the seed as crystal growth occurs.

Following is a specific example of how to practice the invention using the apparatus of FIGS. 1–4.

EXAMPLE

A molybdenum crucible having an internal diameter of about 1½ inch, a wall thickness of about 3/16 inch, and an internal depth of about 1¼ inch is positioned in the furnace in the manner shown in FIGS. 1 and 2. Disposed in the crucible is a die assembly constructed generally as shown in FIGS. 2 and 3. The outside dimensions of surface 44 of rod 38 are ⅝ inch by ¼ inch; the inside dimensions of surface 44, i.e. the cross-sectional dimensions of bore 40, are ½ inch by ⅛ inch. The length of rod 38 is such that its upper end projects about 1/16 inch above the crucible. 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 24 grown previously by the EFG technique is mounted in chuck 22. Tube 24 is straight and conforms in cross-section to the shape and size of end surface 44 of rod 38. Tube 24 is mounted in chuck 22 so that it is aligned axially with pulling rod 20 and also rod 38. The furnace housing 4 is evacuated and filled with argon via lines 8 and 10 to a pressure of about 1 atmosphere which is maintained during the growth period. Then the RF coil 6 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 44 reaches a temperature of about 2070° C. As the solid alumina is converted to the melt 27, columns of melt will rise in and fill capillaries 46. After affording time for temperature equilibrium to be established, the pulling mechanism is actuated and operated so that the seed tube 24 is moved into contact with the upper surface 44 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 48 which fully covers surface 44 and connects with the columns of melt in the capillaries. After about 60 seconds, the seed 24 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, propagating vertically throughout the entire horizontal expanse of the film, with the result that the growing crystal conforms in cross-sectional area and shape to surface 44. The film's surface tension causes additional melt to flow out of the capillaries to maintain the volume of the film constant. After about 2 minutes of pulling the tube, the pulling mechanism is caused to commence rotation of the pulling rod and to maintain such rotation at an angular velocity of about 2 degrees/min. The translational pulling speed is held constant at about 0.2 in./min. Notwithstanding rotation of the seed, crystal growth continues from the full expanse of the film, but as growth proceeds the growing crystal undergoes a rotational transformation so that it appears twisted as illustrated in FIG. 5. Growth is continued without any change in translational or pulling speed until the crystalline extension on the seed has grown to the desired length, whereupon the translational pulling speed is immediately increased to about 1.0 in./min., whereby the growing body pulls free of film 48. Thereafter the furnace is cooled and seed 24 retrieved from chuck 22. The extension grown on the tube is found to have a cross-sectional configuration conforming in shape to end surface 44 of the die assembly with a wall thickness of about 1/16 inch. Additionally the extension is characterized by a spiral twist. The grown crystal is essentially monocrystalline and is a crystallographic extension of the crystal lattice of seed tube 24.

It is to be noted that if the operating temperature (as determined by the average temperature of film 48) 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 degrees with respect to the melting point of alumina) without any substantial change in the cross-section of the grown crystal.

Essentially the same operating conditions as those set forth in the preceding Example may be employed in growing essentially monocrystalline alumina bodies with the apparatus of FIGS. 6, 7, 9 and 11–13 according to the procedures described above for growing bodies of the type shown in FIGS. 8, 10 and 14. Furthermore, bodies characterized by other cross-sectional shapes, e.g. solid rods or tubes of hexagonal, square or triangular shapes, rods having a plurality of longitudinally extending bores, etc. may be grown with a rotational transformation in accordance with this invention. Thus by replacing rod 38 of FIGS. 2 and 3 with a rod having two or more round axial bores instead of bore 40, it is possible using the procedure of the foregoing Example to grow a flat rod of single crystal alumina having two or more axial bores.

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 ruby, spinel, beryllia, barium titanate, yttrium aluminum garnet, lithium niobate, lithium fluoride and calcium fluoride. With respect to such other materials, the process is essentially the same as that described for alpha-alumina, except that it requires different operating temperatures because of different melting points and different seed crystals selected according to the material to be grown. Additionally, certain minor changes may be required in the apparatus e.g., different crucible and die materials selected according to the reactivity and melting points of the melt material.

Laue X-ray back reflection photographs of 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 with in 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 "essentially 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.

With respect to the die assembly, it is to be understood that as used herein the term "end surface" is intended to cover the effective film-supporting surface of the die, and the term "capillary" is intended to denote a passageway that can take a variety of cross-sectional forms such as rectangular bores or an annular space. The term "effective film-supporting surface" denotes the end surface of the die, e.g., surface **44**, as it would appear if the capillary opening or openings, e.g., capillary **46**, were omitted, since when a film fully covers the end surface it extends over the capillary openings. It is to be understood also that the term "rotational transformation" is intended to encompass shapes of the type shown in FIG. 14 as well as those of the type shown in FIGS. 5, 8, and 10.

The significant advantage of the invention is that it makes it possible to grow essentially monocrystalline bodies in a variety of complex geometric shapes for different uses. Thus, for example, it is possible to grow ceramic Bourdon tubes for use in making pressure transducers for high temperature applications. Similarly, if the rod **38C** of FIG. 13 is modified so that its upper surface **44C** has the shape of an air cross-section, it is possible with the apparatus of FIGS. 11 and 12 to grow a curved body similar to that of FIG. 14 except that its cross-section will be like that of an air foil. Such a body, if made of a high temperature material, is adaptable for use as a turbine blade.

What is claimed is:

1. Method of growing from a melt of a selected crystalline material an essentially monocrystalline body of complex shape having a predetermined cross-sectional configuration and a predetermined curvilinear transformation of said cross-sectional configuration lengthwise of said body, said method comprising:

establishing a thin liquid film of said selected material on and substantially fully covering a nonliquid substantially horizontal surface that terminates in sharp edges and has an edge configuration conforming to said predetermined cross-sectional configuration, the surface tension of said film being such as to prevent said film from overrunning said sharp edges;

controlling the temperature of said film so that it has a temperature gradient along its depth with the film being hottest at said surface;

growing and pulling an essentially monocrystalline body from the cooler side of said film at a selected rate with growth occurring by successive accretions of solid at all points along the horizontal expanse of the interface of said body and said film;

simultaneously rotating said body at a rate at which adherence of said film to said body and growth of said body can subsist about a predetermined axis which is located so that successive accretions of solid cause said body to acquire a complex shape that is characterized by said predetermined cross-sectional configuration and a curvilinear transformation of said predetermined cross-sectional configuration lengthwise of said body; and

simultaneously supplying an additional quantity of said selected material in liquid form to said surface via at least one opening in said surface to replace the liquid consumed in growing said body from said film.

2. Method according to claim **1** wherein said substantially horizontal surface has a continuous outside edge and at least one continuous inside edge and said body is rotated on a vertical axis.

3. Method according to claim **1** wherein said substantially horizontal surface has a polygonal edge configuration and said body is pulled vertically away from said film.

4. Method according to claim **2** wherein said body is pulled along said vertical axis.

5. Method according to claim **2** wherein said body is pulled vertically along an axis displaced laterally from said vertical axis.

6. Method according to claim **2** wherein at least one of said inside and outside edges has a polygonal configuration and said body is pulled along said vertical axis.

7. Method according to claim **1** wherein said body is rotated about a horizontal axis.

8. Method according to claim **1** wherein said substantially horizontal surface has a circular outside edge and said body is pulled vertically along an axis displaced laterally from said vertical axis.

9. An elongate essentially monocrystalline body having (1) a longitudinal axis, (2) a predetermined arbitrary cross-section, and (3) a longitudinally extending inner surface characterized by a rotational transformation relative to said longitudinal axis.

10. An elongate essentially monocrystalline body having a predetermined arbitrary cross-section and a transformation of said cross-section along a selected axis.

11. A body according to claim **10** wherein said cross-section is rotationally transformed about an axis extending in the same direction as the longitudinal geometric axis of said body.

12. A body according to claim **10** wherein said cross-section is rotationally transformed about the geometric axis of said body.

13. A body according to claim **10** wherein said cross-section is rotationally transformed about an axis that is exterior to said body.

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