United States Patent [19]

Vichr

[11] **3,915,661**

[45] **Oct. 28, 1975**

[54] **PROCESS AND APPARATUS FOR GROWTH OF CRYSTALS**

[75] Inventor: **Miroslav Vichr**, Cedar Knolls, N.J.

[73] Assignee: **Allied Chemical Corporation**, New York, N.Y.

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[52] **U.S. Cl.** ..... **23/301 R**; 23/273 R; 23/286; 423/263; 423/594

[51] **Int. Cl.**[2] **B01J 17/20**

[58] **Field of Search** ..... 23/273 R, 301 R, 269, 286

[56] **References Cited**

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Primary Examiner—James H. Tayman, Jr.
Attorney, Agent, or Firm—Arthur J. Plantamura; David W. Collins; Jack B. Murray, Jr.

[57] **ABSTRACT**

Process and apparatus are provided for the growth of large, defect-free crystals from a flux comprising a solvent saturated with dissolved crystal-producing material. The large, defect-free crystals are grown by providing a crucible with crystal-producing material held in an apertured enclosure in the bottom and partially filling the crucible with flux. A seed crystal is attached to the crucible, above the apertured enclosure and the flux. Upon heating to temperature sufficient to induce crystal growth, the flux becomes saturated with the crystal-producing material. The crucible is then inverted and the saturated flux is brought in contact with the seed crystal. The temperature is then gradually reduced to induce crystal growth. At the completion of crystal growth, the crucible is reinverted and the grown crystal is harvested.

4 Claims, 4 Drawing Figures

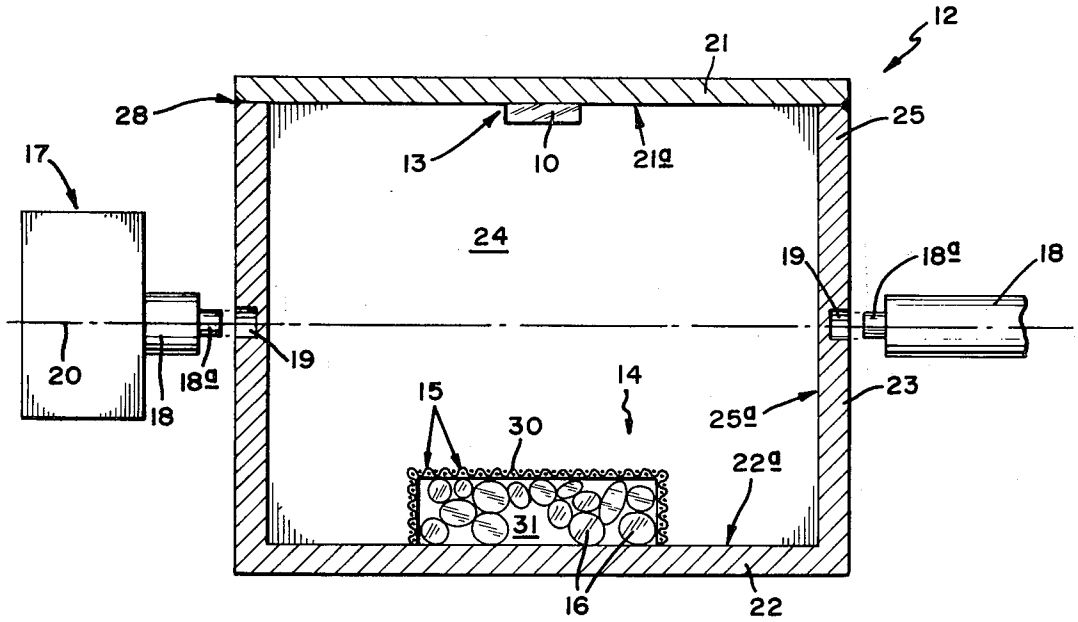


FIG. 1

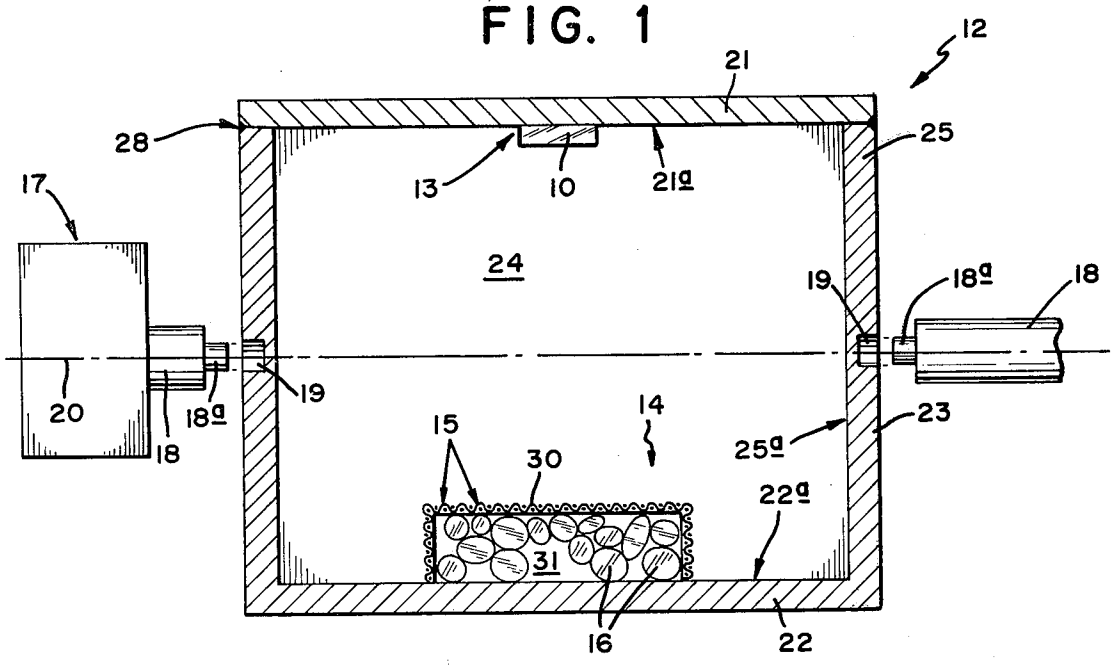

12
21
28
25
13
10
21a
17
24
19
18a
18
20
18a
19
14
15
30
25a
23
22a
31
16
22

FIG. 2

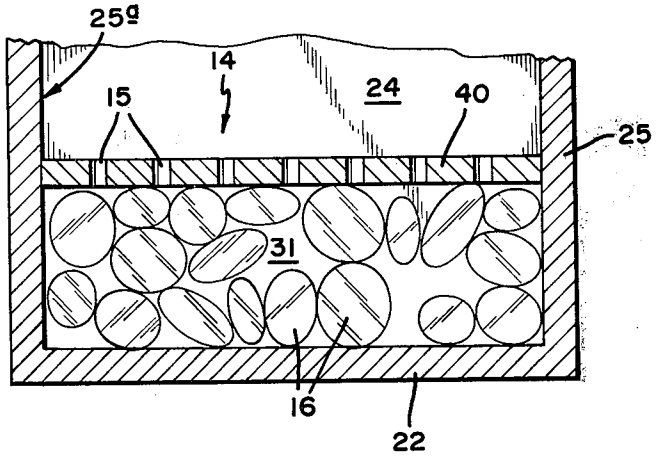

25a
14
15
24
40
25
31
16
22

FIG. 3

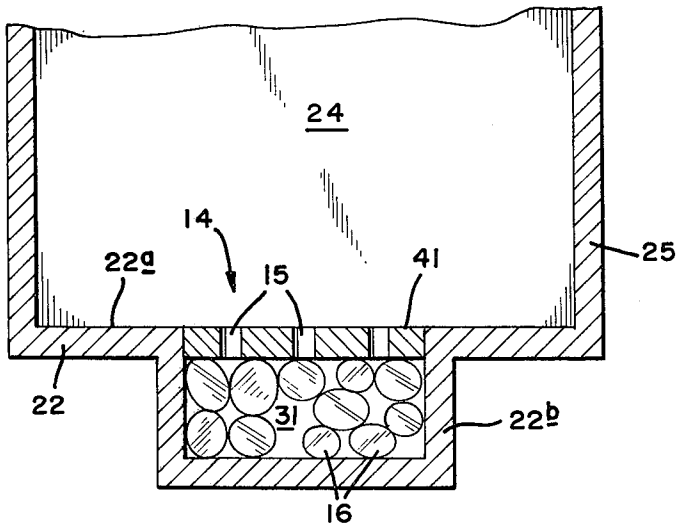
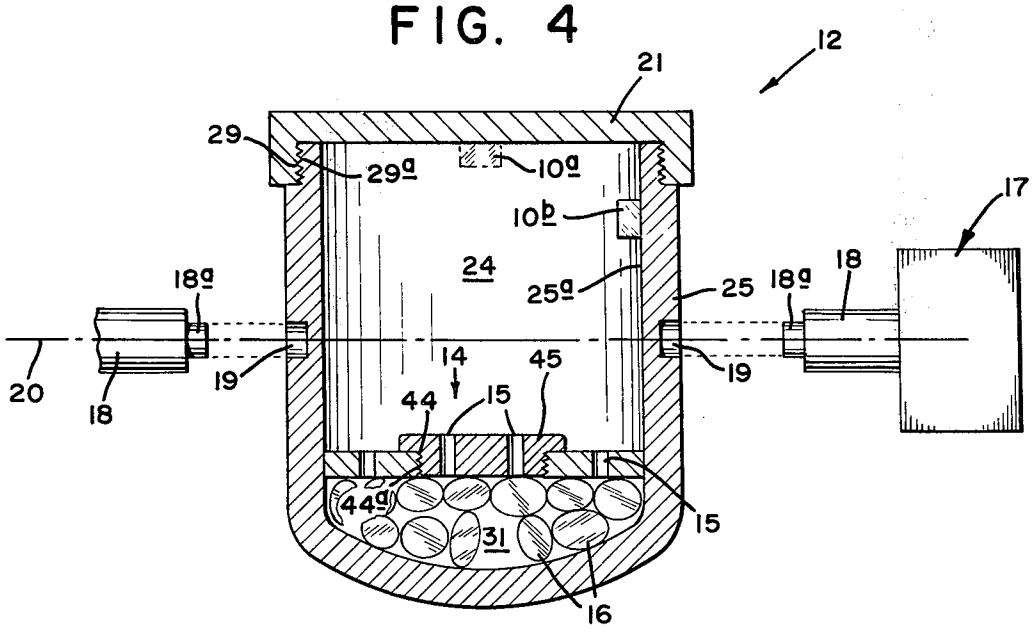

24
14
22a
15
41
25
22
31
22b
16

FIG. 4


12
21
29
29a
10a
10b
17
24
18a
25a
25
18a
18
20
18
19
14
45
19
44
15
44a
15
31
16

PROCESS AND APPARATUS FOR GROWTH OF CRYSTALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the growth of crystals and more particularly to the growth of crystals from a flux containing crystal-producing material.

2. Description of the Prior Art

With the increased use of crystals by science and industry, an economical and efficient method for the growth of defect-free crystals is desirable. The growth of crystals from a high temperature solution or flux, whereby single crystals are formed by cooling a solution comprising a solvent containing crystal-producing material dissolved therein, has generally been found to yield non-strained crystals with a lower concentration of point defects than are produced by a method of crystallization by direct freezing from a melt.

Growth of crystals from a flux is particularly adapted to the obtainment of crystals of (1) materials such as Fe_2O_3 and YVO_4 which decompose on melting (2) materials which have a high vapor pressure at their melting point, such as ZnS, or (3) materials such as yttrium iron garnet ($Y_3Fe_5O_{12}$) and $AlVO_4$ which are incongruently melting and which therefore cannot be grown from their own melts. To avoid spontaneous nucleation of crystals on the inner surface of a container containing such a flux, and to thereby minimize the undesired growth of many small crystals, a seed is typically employed to obtain large crystals by the provision of the seed as a principal nucleation site.

Methods and apparatus for the flux growth of crystals employing crucible inverting techniques are well known. See, e.g. W. Tolksdorf, "Growth of Yttrium Iron Garnet Single Crystals," Journal of Crystal Growth 3, 4, p. 463 (1968) and G. A. Bennett, "Seeded Growth of Garnet From Molten Salts," Journal of Crystal Growth 3, 4, p. 458 (1968). In conventional apparatus, a seed is attached to the inner surface of the top of crucible. A measured quantity of solid crystal-producing material and solvent for the material is introduced into the crucible, which is sealed, heated to the desired temperature and then inverted to bring the heated flux into contact with the seed. The temperature of the crucible is then slowly lowered so as to initiate crystal growth upon the seed. At the selected final temperature, i.e. the "final growth temperature", the container is reinverted so as to drain the flux from the resulting crystal. The crucible is then opened to remove the crystal and additional raw material is added to the flux in order to replace material which has been incorporated into the crystal.

While large crystals are obtained by the use of such apparatus, it is necessary to know with a great deal of precision the solubility of the selected crystal-producing material in the solvent employed in order to prevent either (1) the dissolution of the seed crystal upon its initial contact with a flux which is not saturated with the crystal-producing material or (2) the growth of numerous small crystals due to the presence of undissolved solids in the flux during the period of crystal growth. Because of the great difficulties involved in accurately determining solubilities in high temperature fluxes and because seed crystals are usually very small since they are normally obtained from spontaneously nucleated runs, seeding operations have a very high percentage of failure due to the complete dissolution of the seed. Thus, dissolution of the seed crystals is a recurrent and serious economic problem in the growth of crystals from a flux.

SUMMARY OF THE INVENTION

According to the present invention, large defect-free crystals are grown from a flux comprising a solvent saturated with crystal-producing material by a process which comprises: partially filling an enclosable container provided with an apertured enclosed zone containing solid crystal producing material with a solvent having the ability to dissolve said solid crystal-producing material, thereby contacting said solids with said solvent, said container having a seed attached to the inner surface thereof for crystal growth thereon, said seed being positioned in said container above said apertured enclosed zone and said solvent; heating said solvent to attain saturation thereof with the crystal-producing material, thereby forming a saturated flux; inverting said container to drain said saturated flux from said apertured enclosed zone, thereby contacting said seed with said saturated flux; cooling said saturated flux to effect crystal growth upon said seed; and reinverting said container to drain flux depleted of crystal-producing material from said seed and said crystal grown thereon. One or more series of crystal growth steps may be carried out whereby the depleted flux is heated again to resaturate the solvent with crystal-producing material and the container inverted, cooled and reinverted to attain further crystal growth.

The apparatus of the present invention comprises: an enclosable container provided with apertured means for enclosing solid crystal-producing material therein; means for attaching a seed to the inner surface of said container above said apertured means for crystal growth on said seed; and means for inverting said container.

The process and apparatus of the present invention have the significant advantage of allowing the growth of large defect-free crystals without the necessity of opening the container to replenish the flux with the crystal-producing material which has been incorporated into the grown crystal, thereby enabling the growth of larger crystals than have heretofore been obtained. In addition, by the process and apparatus of the present invention, crystals may be grown from a flux without the need for a precise knowledge of the solubility of the crystal-producing material in the solvent selected for use, thereby significantly reducing both the dissolution of seed crystals and the undesired growth of numerous small crystals which have otherwise been serious problems for solvent/crystal-producing material systems for which such solubilities are not known with the requisite precision. Therefore, the present invention has the significant economic advantage of enhancing the efficiency of crystal growth for a wide variety of solvent/crystal-producing material systems.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of an embodiment of the apparatus of the present invention.

FIG. 2 is a cross-sectional view of a portion of the container illustrating an altervative structure thereof.

FIG. 3 is a cross-sectional view of a portion of the container illustrating another alternative structure thereof.

FIG. 4 is a cross-sectional view of another embodiment of the apparatus of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to FIG. 1, an embodiment of the apparatus of the present invention is illustrated which comprises: container, indicated generally at 12, having cover 21, bottom 22 and sides 25; means indicated generally at 13, for attaching seed 10 to inner surface 21*a* of cover 21 for crystal growth thereon; apertured means, indicated generally at 14, for enclosing solid crystal-producing material 16 therein; and means, indicated generally at 17, for inverting container 12. As used herein, the terms "inverting" and "inversion" are intended to mean the rotating of container 12 to reverse the relative vertical positions of cover 21 and bottom 22.

The process and apparatus of the present invention may be employed to grow a wide variety of crystals from the flux. Crystal-producing materials which may be employed are conventional and include, as for example, yttrium vanadate, aluminum oxide, iron oxide, yttrium iron garnet ($Y_3Fe_5O_{12}$) and magnetic spinels such as metal ferrites, e.g. magnesium ferrite and nickel ferrite. Especially preferred as crystal-producing materials in the present invention are YVO_4 and yttrium iron garnet ($Y_3Fe_5O_{12}$). The crystal-producing materials which are employed may be obtained from conventional sources as, for example, crystal fragments or polycrystalline sintered ceramics. The selected solid crystal-producing material is preferably of a particle size which is at least three times greater than the largest aperture in apertured means 14, thus preventing solids 16 from escaping therefrom. For example, when apertured means 14 comprises a 20 mesh screen, solids 16 are preferably from about 3 mm to 6 mm in size. However, since the process and apparatus of the present invention are particularly adapted to the growth of large crystals through the use of a number of growth cycles, the selected solid crystal-producing material is most preferably of a particle size which is at least about six times greater than the opening formed by the largest aperture 15 in apertured means 14.

The amount of solid crystal-producing material 16 which is employed in container 12 must be sufficient to saturate the volume of solvent which is employed at the selected initial temperature. The amount of solid crystal-producing material necessary to effect saturation of the solvent will, of course, vary depending on the solvent/crystal-producing material system selected for use, but is generally from about 20 to 200 grams of solid crystal-producing material per 100 grams of solvent, and preferably from about 20 to 80 grams of solid crystal-producing material per 100 grams of solvent. Solids 16 are generally present in an amount sufficient to occupy from about 5 to 70 percent by volume, and preferably from about 30 to 70 percent by volume, of chamber 31 formed by apertured means 14, e.g. housing 30 in the apparatus of FIG. 1.

Seed 10, serves as the primary nucleation site upon which crystal-producing material is deposited for crystal growth and is preferably a crystal having the composition of that crystal desired to be grown in container 12. The size of seed 10 may vary widely. Generally, however, since the initial rate of crystal growth, and the number of crystal imperfections, decreases as the size of seed 10 increases, seed 10 is preferably a large crystal so as to attain a grown crystal having the fewest imperfections. While single seed 10 is generally employed, two or more seeds may be used to grow two or more crystals according to the process of the present invention.

Seed 10 is attached to an inner surface of container 12, e.g. inner surface 21*a* of cover 21 as illustrated in FIG. 1. Alternatively, as illustrated in FIG. 4, seed 10 may be attached to inner surface 25*a* of wall 25. However, seed 10 must be positioned above apertured means 14, and also above the liquid level of solvent contained in container 12 (when container is in its original position) to allow solvent to contact solid crystal-producing material 16 in apertured means 14 without simultaneously contacting seed 10.

The solvent employed must be liquifiable and have the ability to dissolve the selected crystal-producing material, and, in addition, should possess a melting point lower than the melting point of the selected solid crystal-producing material. Thus, while the particular solvent selected for use depends on the selected crystal-producing material, the temperatures to be employed, the toxicity, availability and stability of the solvent, and other factors, solvents which are conventionally used include, for example, metal oxides, such as PbO and Bi_2O_3; other oxides such as B_2O_3; metal fluorides such as PbF_2; and mixtures thereof. Solvent/crystal-producing material systems which may be employed are conventional and include, as for example, those disclosed in U.S. Pat. Nos. 2,848,310, 3,079,240, and 3,386,799.

The selected solvent may be introduced into the apparatus of the present invention either as a solid or as a liquid. Thus, a solvent which at room temperature and atmospheric pressure is a solid may also be introduced to container 12 as a liquid when the selected solvent is heated to a temperature in excess of its melting point prior to its introduction into container 12.

The amount of solvent which is employed must be sufficient to dissolve at least a portion of the selected crystal-producing material introduced into container 12. While the precise amount of solvent selected for use varies widely depending on the solubility therein of the selected crystal-producing material, the temperatures employed, and other factors, the amount of solvent employed should be less than that amount of solvent which would contact seed 10 and apertured means 14 simultaneously either when container 12 is in either its original position, i.e. when cover 21 is uppermost with respect to bottom 22, or its inverted position, i.e. when bottom 22 is uppermost with respect to cover 21. The amount of solvent which would so contact seed 10 and apertured means 14 also varies depending on the amount by which the fluid volume increases, due to the dissolution of solids 16 in the selected solvent, over that fluid volume attributable only to the solvent employed. Generally, however, the selected solvent is employed in an amount of from about 0.5 to 5 grams of solvent per gram of solid crystal-producing material introduced into the apparatus of the present invention, and preferably from about 1.25 to 5 grams of solvent per gram of solid crystal-producing material.

Container 12 and chamber 24 defined thereby may be symmetric or asymmetric and thus may be of various geometric shapes, such as for example, cylindrical, spherical, triangular and the like with the cylindrical shape being preferred. Container 12 may be composed

of any material which is non-reactive with any component of the flux under the conditions of crystal growth employed, and which is capable of withstanding the temperatures and rotations employed in the present invention. Such container materials are conventional and include metals such as platinum and iridium, with platinum being preferred. Alternatively, container **12** may be provided with an inner coating of platinum or of another material which is non-reactive with the flux components, and an outer coating not in contact with the flux such as stainless steel or iridium for structural strength. In addition, container **12** should be capable of being sealed so as to prevent the escape of flux therefrom. Various methods are known to the art for sealing such containers, with sealing as by welding being most preferred. When, as is preferred, container **12** is sealed by welding thereon cover **21,** welded seal **28** is formed. Of course, seal **28** may be removed by known methods at the completion of a given growth cycle to open container **12** so as to remove crystals grown therein and to replenish solid crystal-producing material **16.**

While not critical, the inner surfaces of container **12,** which surfaces comprise inner surface **21***a* of cover **21,** inner surface **22***a* of bottom **22** and inner surface **25***a* of sides **25,** are preferably smooth and substantially without bumps, ridges, cavities or other structural inhomogeneities, thereby minimizing the number of sites upon which crystal growth spontaneously nucleates and increasing the efficiency of the growth of large crystals on seed **10.** Surfaces **21***a*, **22***a* and **25***a* may be flat, as is illustrated in FIG. **1** for cylindrical chamber **24.** Alternatively, as where chamber **24** is defined by container **21** to be of a geometric shape such as spherical, inner surfaces **21***a*, 22*a* and **25***a* may be curved.

Means, indicated generally at **13,** for attaching seed **10** to cover **21** may comprise various seed attaching means known to the art, such as, for example, affixing seed **10** by thin wires which are welded to inner surface **21***a* and which are composed of a material such as platinum, capable of withstanding the temperatures employed and non-reactive with components of the flux. Apertured means **14** is positioned within container **12** so as to allow solvent to contact at least a portion of solid crystal-producing material **16** enclosed in apertured means **14** without simultaneously contacting seed **10.** While most efficient use of container **12** would require apertured means **14** to be positioned only in the bottommost portion of container **12,** a portion of apertured means **14** may also be positioned in the uppermost portion of container **12** so long as the above constraints are met, i.e. so long as the solvent does not simultaneously contact seed **10** and solids **16** enclosed in apertured means **14.**

In the embodiment of FIG. **1,** apertured means, indicated generally at **14,** for enclosing solid crystal-producing material **16** comprises housing **30** which, as is most preferred, comprises a screen attached to bottom **22.** Housing **30,** which comprises the apertured enclosed zone in the apparatus of FIG. **1,** defines chamber **31** and is provided with apertures, indicated generally at **15,** communicating chamber **31** with chamber **24** to allow solid crystal producing material **16** to be contacted by solvent in container **12** when the container is in its original position for dissolution of solids **16** in said solvent.

Alternatively, apertured means **14** may comprise one or more baffles which are positioned in container **12** so as to cooperate with the inner surfaces of container **12** to define a chamber for enclosing solids **16.** Thus, in FIG. **2,** which illustrates another embodiment of the apparatus of the present invention, a portion of container **12** is shown wherein apertured means **14** comprises baffle **40** attached to inner surface **25***a* of sides **25,** thereby cooperating with sides **25** and bottom **22** to define chamber **31** for enclosing solid crystal-producing material **16.** Baffle **40** is provided with apertures **15** which communicate chamber **31** with chamber **24** to allow solids **16** to be contacted by solvent in container **12.**

FIG. **3,** illustrating yet another embodiment of the apparatus of the present invention, shows a portion of container **12** wherein apertured means **14** comprises baffle **41** which is attached to inner surface **22***a* of bottom **22** and which cooperates with recess **22***b* of bottom **22** to define chamber **31** enclosing solid crystal-producing material **16.**

Apertured means **14** may be attached to an inner surface of container **12** by conventional means, as by welding or through use of platinum wires which are in turn welded to an inner surface, e.g. inner surface **22***a*. Apertures **15** are sufficiently large and numerous to allow flux to flow freely into chamber **31** but are preferably not so large as to allow solids **16** to escape from their respective chambers into chamber **24.** While a single aperture **15** is sufficient to effect contact of seed **10** with the selected solvent, preferably at least about **10** apertures are employed, and most preferably at least **100** apertures. Especially preferred as apertured means in the present invention are **20** mesh platinum screens.

Apertured means **14** may be composed of any material which is non-reactive with any component of the flux, which is compatible with the material of which container **12** is composed, which is able to withstand the temperatures employed and which has sufficient structural strength to support the weight of solid crystal-producing material **16** when container **12** is in its inverted position. Typical of materials of construction which may be employed are platinum or other noble metals. An especially preferred material of construction is platinum.

Container **12** is provided with means, indicated generally at **17,** for inverting container **12** about horizontal center axis **20.** Any of the conventional methods of effecting inversion of containers may be employed as inversion means **17.** Thus, for example, container **12** may be suitably supported for rotation in shafts **18** which interlock with container **12** by means of the reduced portion **18***a* which may comprise a sprocket or other similar construction capable of meshing with cavity **19** in container **12.** Suitable motor or drive means to rotate shaft **18** may be connected thereto. Locking cavities **19** are preferably of a depth in outside wall **23** of container **12** which does not substantially reduce the structural strength of container **12** and which does not allow the escape of either atmosphere or flux from chamber **24.**

Alternatively, as is preferred, container **12** may be housed in a conventional ceramic crucible provided with a lid to secure container **12** therein and locking cavities in the crucible walls which cooperate with rotating arms **18,** in like manner as described alone with respect to locking cavities **19,** for inversion of container **12.**

In FIG. **4** is illustrated still another embodiment of the apparatus of the present invention wherein cover

21 is secured by suitable means to effect a tight seal. For example, cover 21 is provided with internal threads 29 which cooperate with corresponding external threads 29*a* in wall 25 to allow cover 21 to be removed for access to inner chamber 24 of container 12, thereby eliminating the need for sealing container 12 by welding. Seed 10*b* is attached to inner surface 25*a* of wall 25 above apertured means 14 which comprises baffle 41*a*, attached as by welding to surface 25*a*, and threaded cap 45. Cap 45 is provided with external threads 44 which cooperate with corresponding internal threads 44*a* in baffle 41*a* to allow cap 45 to be removed for access to inner chamber 31 wherein solid crystal-producing material 16 is enclosed. Both baffle 41*a* and threaded cap 45 are provided with apertures 15 to provide for the passage of solvent into chamber 31 to contact solid crystal-producing material 16. Seed 10*a*, attached to inner surface 21*a* of cover 21, may be optionally employed, alone or in combination with seed 10*b*.

In operation of the apparatus of FIG. 1, a desired quantity of solid crystal-producing material 16, e.g. YVO_4, is introduced into apertured means 14, i.e. housing 30, which is then positioned within container 12 as by welding to inner surface 22*a*. The selected amount of solvent, e.g. a mixture of Bi_2O_3, $NaVO_3$ and V_2O_5, is then introduced into container 12, partially filling said container. With container 12 in its original position (so as to allow the liquefied solvent to contact solid crystal-producing material 16) the solvent is then heated to the initial temperature, which is a temperature greater than the melting point of the selected solvent (so as to liquefy the solvent) but less than the boiling point of the flux and which is preferably less than the melting point of the selected solid crystal-producing material 16.

while the precise temperatures employed in the process of the present invention may vary widely depending on the crystal-producing material and solvent selected for use and other factors, for high temperature crystal growth the initial temperature is generally between about 600° and 2,000°C., and preferably between about 1,000° and 1,400°C. The use of as high temperature an initial temperature as possible is preferred to minimize the period of time required for the solvent to become saturated with crystal-producing material, since, for most solvent/crystal-producing material systems, the rate of dissolution of solids 16 in the solvent increases with increasing temperature.

Container 12, which may be heated by conventional means, such as by induction coils or by silicon carbide heating elements, is preferably heated to the initial temperature at a rate of from about 50° to 500°C./hr., although faster or slower rates of heating may be employed without adverse results.

when the selected initial temperature is reached, container 12 is maintained at this temperature for a period of time (the "saturation period") sufficient to ensure saturation of the flux with crystal-producing material before container 12 is inverted to contact seed 10 with the saturated flux.

The saturation period varies widely depending on the crystal-producing material and solvent selected for use, the initial growth temperatures employed, the particle size of solid crystal-producing material 16, and other factors, but is generally from about 5 to 50 hours, and preferably from about 10 to 20 hours.

At the end of the saturation period, container 12 is inverted, thereby draining the saturated flux from solid crystal-producing material 16 and contacting seed 10 with the saturated flux. Container 12 is then cooled to initiate crystal growth of seed 10, thereby reducing the concentration of crystal-producing material remaining dissolved in the solvent. The rate of cooling of container 12 during the period of crystal growth may vary widely and is generally from about 0° to 50°C./hr. and preferably between about 0.5° and 2°C./hr. Thus, for a solvent/crystal-producing material system which employs an initial growth temperature of 1,300°C. and a final growth temperature of 1,000°C., the growth period is preferably from about 150 to 600 hours in length.

At the final growth temperature, i.e. the lowest temperature at which crystal growth is desired, container 12 is reinverted, completing the first growth cycle, thereby bringing container 12 to its original position, draining from seed 10 and the crystal grown thereon the solvent having a reduced concentration of crystal-producing material dissolved therein (i.e. the "depleted flux") and contacting apertured means 14 with the depleted flux for dissolution of additional solid crystal-producing material 16 therein.

While most efficient use of the apparatus of the present invention would require that as much of the crystal-producing material dissolved in the solvent be incorporated into the grown crystal during a given growth period as is possible (consistent with phase equilibria), the present invention may be practiced to incorporate any portion of dissolved crystal-producing material in the grown crystal during a given growth cycle.

The final growth temperature may also vary widely depending on the crystal-producing material and solvent selected for use, the percent of dissolved solids desired to be incorporated in the grown crystal, and other factors, but is generally from about 500° to 1,700°C., and preferably from about 700° to 1,000°C. In any event, the final growth temperature should be greater than the freezing point of the flux containing the selected solvent and crystal-producing material, so as to prevent the solidification of the flux about the seed and crystal, which would greatly complicate the recovery of the grown crystal from container 12.

In its original position, container 12 is again heated to the selected initial temperature and is maintained at this temperature for a period of time to ensure resaturation of the flux with solid crystal-producing material 16. The period of time ("resaturation period") necessary to effect resaturation of the depleted flux after the first or a succeeding growth cycle varies greatly depending on the percent of crystal-producing material in the flux which is incorporated in the growing crystal during the preceding growth cycle, the temperature employed, the particular solvent, the crystal-producing material selected for use and other factors. Generally the resaturation period is from about 5 to 50 hours, and preferably from about 10 to 20 hours.

At the end of the resaturation period, container 12 may again be inverted, cooled, and reinverted as above, so as to effect additional crystal growth upon seed 10 and the crystal grown thereon during the preceding growth cycle. The above growth cycles may be repeated by continued resaturation of the flux by inversion of container 12 after each period of crystal growth until the particle size of crystal-producing material 16

remaining within apertured means **14** is 1.5 times larger than the largest aperture **15** employed.

While the apparatus and process of the present invention are particularly adapted for providing large crystals by the use of a number of growth cycles without the requirement of opening container **12,** this is not to be considered as limiting, and the process and apparatus of the present invention are also directed to a single growth cycle. Thus, it is not critical to the present invention that container **12** be opened only when the particle size of solid crystal-producing material **16** remaining in apertured means **14** is 1.5 times larger than the largest aperture **15.**

After the first or any succeeding growth cycle, container **12** is cooled in its origitnal position to room temperature, generally at a rate of cooling of from about 10° to 100°C./hr. and preferably 20° to 50°C./hr. After container **12** has been cooled to room temperature, the container is opened, such as by removing welded seal **28** so as to separate therefrom cover **21** in the apparatus of FIG. **1.** Seed **10** having the crystal grown thereon is then removed from cover **21.** Container **12** may be heated while cover **21** is so removed to liquify any solid flux contained therein, thereby allowing access to apertured means **14** for addition thereto of additional solid crystal-producing material **16** for reuse of container **12.**

As will be apparent to a skilled practitioner, the initial temperature and the final growth temperature employed during the second or any succeeding growth cycle need not be the same as that selected for use in any preceeding growth cycle, e.g. the first growth cycle.

Container **12,** by conventional means, may be optionally subjected to accelerated and decelerated rotation about the vertical axis of container **12** to provide for enhanced mixing of the flux components and to thereby increase both the rate of dissolution of solid crystal-producing material **16** in the selected solvent and the rate of crystal growth from the saturated flux. A typical rotational mixing method is that disclosed in H. J. Scheel, "Accelerated Crucible Rotation: A Novel Stirring Technique in High-Temperature Solution Growth," Journal of Crystal Growth, 13/**14, 560**–565 (1972). Where employed, accelerated/decelerated mixing rotation is generally at an acceleration of from about 18 to 1,800 revolutions per minute^2, and preferably from about 180 to 600 revolutions per minute^2.

A venting tube may be optionally employed to equalize the pressure within chamber **24** with that of the atmosphere so as to prevent the build-up of pressure during heating. Where employed, the venting tube is preferably attached to inner surface **21***a* so as to communicate chamber **24** with the atmosphere. The tube may be of various geometric shapes, with a substantially S-shape being preferred, and may be constructed of any material capable of withstanding the temperatures employed and non-reactive with any component of the flux. Such materials of construction are conventional and include platinum and iridium. Preferably, the evaporation tube is positioned so that the plane in which it lies is perpendicular to that formed by the axis about which container **12** is rotated for inversion, designated as center horizontal axis **20** in the apparatus of FIG. **1.**

When the apparatus of the present invention employs a venting tube which is positioned as discussed above, rotation means **17** for inverting container **12** is preferably adapted to selectively rotate container **12** about axis **20** in both the clockwise or counterclockwise directions, with reference to the plane formed by the evaporation tube. Thus, when container **12** is rotated either from its original position to its inverted position, or vice versa, container **12** is preferably rotated about axis **20** in the direction which prevents or minimizes the escape of fluid through the evaporation tube.

The process and apparatus of the present invention may be further illustrated by reference to the following examples:

EXAMPLE 1

To the apparatus of FIG. **1,** which comprises a cylindrical 1,000 ml. platinum container, is introduced (1) 2,250 grams of a solvent consisting of 73 weight percent Bi_2O_3, 26 weight percent $NaVO_3$ and 1 weight percent V_2O_5; and (2) crystal-producing material comprising 500 grams of YVO_4 in the form of crystal fragments, having an average weight of 5 grams, which is housed in a 20 mesh platinum screen which is attached by welding to the bottom inner surface of the container. The container is then sealed by welding thereon a platinum cover having 30 grams YVO_4 seed attached to the inner surface of the cover.

The container is heated at a rate of 200°C. per hour to the initial temperature of 1,255°C. in a chamber provided with silicon carbide heating elements which maintain a temperature gradient of not greater than 1° over the length of the container. During heating, the container is supported by a verticle pedestal which provides accelerated and decelerated mixing rotation about the vertical axis of the crucible, the rotational acceleration being in the range of 60 to 1,500 revolutions per minute^2. The container in its original position is thus rotated for a period of 24 hours to ensure the saturation of the selected solution with the crystal-producing material, i.e. yttrium vanadate.

At the end of the above **24** hour period, the rotation about the verticle axis of the container is discontinued and the horizontal rotation means is employed to invert the container around its horizontal axis from its original position to its inverted position. The horizontal rotation means is then disengaged whereupon accelerated and decelerated rotational stirring is renewed. The container is cooled at a rate of 0.5° per hour for a period of 810 hours to the final growth temperature of 850°C. so as to initiate crystal growth upon the seed. At the conclusion of the above growth period, the mixing rotation is discontinued and the horizontal rotational means are again employed to rotate the container to its original position, thereby draining the depleted flux from the seed and the crystal grown thereon and contacting the flux with the solid yttrium vanadate enclosed in the platinum screen for resaturation of the flux. After a period of 24 hours with accelerated/decelerated rotational mixing, the container is again rotated about its horizontal axis to its inverted position for repetition of the above growth cycle.

Upon conclusion of the second growth cycle, the container is rotated to its original position whereupon the container is cooled from the final growth temperature (850°C.) to room temperature at a rate of 50°C. per hour. The container is then removed from the furnace and opened. The seed is found to have grown thereon a crystal having a weight of 180 grams, thereby effecting an increase in weight of 150 grams.

By calculation, therefore, it is determined that in each of the above growth cycles, 75 grams of yttrium vanadate crystallized on the seed from 2,250 of solvent. Hence, the difference of solubilities between 1,255°C. and 850°C. is 3.33 grams of yttrium vanadate per 100 grams of flux.

EXAMPLE 2

To the container of Example 1, a solvent consisting of 800 grams PbO, 80 grams B_2O_3, 160 grams Y_2O_3, and 220 grams Fe_2O_3 is introduced as solvent together with 280 grams of polycrystalline yttrium iron garnet as solid crystal-producing material which is placed in the platinum mesh screen. The container is than closed by welding thereon a cover to which a 90 gram seed of yttrium iron garnet is attached. The container is then heated at a rate of 200°C. per hour with accelerated/-decelerated rotational mixing to an initial temperature of 1,250°C. The above initial growth temperature is maintained for a period of 4 hours after which the container is rotated to its inverted position and crystal growth initiated on the seed by cooling the container at a rate of 0.1°C. per hour to a final growth temperature of 1,000°C.

The above growth cycle is repeated after resaturation of the flux. At the end of the above second growth cycle, the crucible is cooled in its original position from the final growth temperature of 1,000°C. to room temperature at a rate of 50° per hour. The container is removed from the furnace and opened, and a crystal having a weight of 276.6 grams is removed therefrom, thereby effecting a 186.6 gram increase in weight over the seed weight employed. Thus, 10.6 grams $Y_3Fe_5O_{12}$ is crystallized from 100 grams of flux.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident to one skilled in the art that various changes and modifications may be made therein without departing from the scope and spirit of the invention. In addition, it will be obvious to the skilled practitioner that one or more of the apparatus of the present invention may be employed in combination with suitable means known to the art to provide automation of the growth of crystals in such apparatus.

I claim:

1. A process for the growth of crystals from a flux comprising a solvent saturated with crystal-producing material which comprises:

a. partially filling an enclosable container provided with an apertured enclosed zone containing solid crystal-producing material with a solvent having the ability to dissolve said crystal-producing material, thereby contacting said solids with said solvent, said solids being present in an amount to ensure saturation upon solvation, said container having a seed attached to the inner surface thereof for crystal growth thereon, said seed being positioned above said apertured enclosed zone and said solvent;

b. heating said solvent to a first temperature sufficient to form a molten body of flux and to attain saturation thereof with said crystal-producing material;

c. inverting said container to drain said saturated flux body from said apertured enclosed zone, thereby immersing said seed in said saturated flux body;

d. cooling said saturated flux body at a controlled rate to a second temperature below said first temperature to effect crystal growth upon said seed; and

e. reinverting said container to drain flux depleted of crystal-producing material from said seed and said crystal grown thereon and to recontact said solids with said solvent.

2. A process according to claim **1** wherein the depleted flux is heated to resaturate said solution with said solid crystal-producing material contained in said apertured enclosed zone, steps (c) and (d) are repeated to supplement the growth on said seed.

3. A process according to claim **1** wherein said container is subjected to accelerated and decelerated mixing rotation concurrent with said steps (b) and (d).

4. An apparatus for the growth of crystals from a flux comprising a solvent saturated with crystal-producing material which comprises:

a. an enclosable container provided with apertured means for enclosing solid crystal-producing material therein;

b. means for heating said enclosable container to a temperature of at least 600°C.;

c. means for attaching a seed to the inner surface of said container above said apertured means and said flux for crystal growth on said seed;

d. means for inverting said container; and

e. means for rotating said container about its vertical axis.

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