Dec. 24, 1968 W. B. CAMPBELL 3,418,076

METHOD FOR CONTROLLING THE FEED OF NUCLEI IN THE PRODUCTION OF CRYSTALS BY VAPOR DEPOSITION

Filed April 14, 1965 2 Sheets-Sheet 1

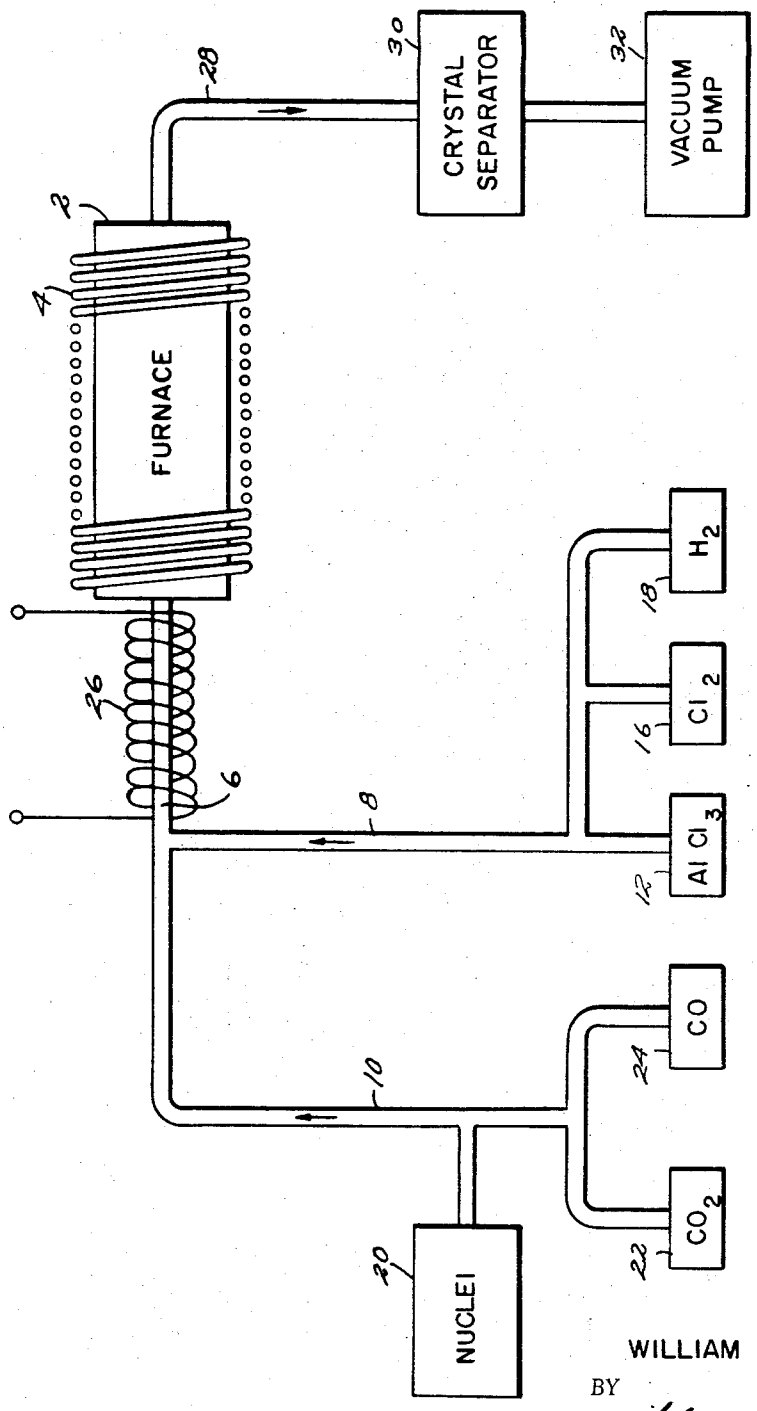


FIG. 1

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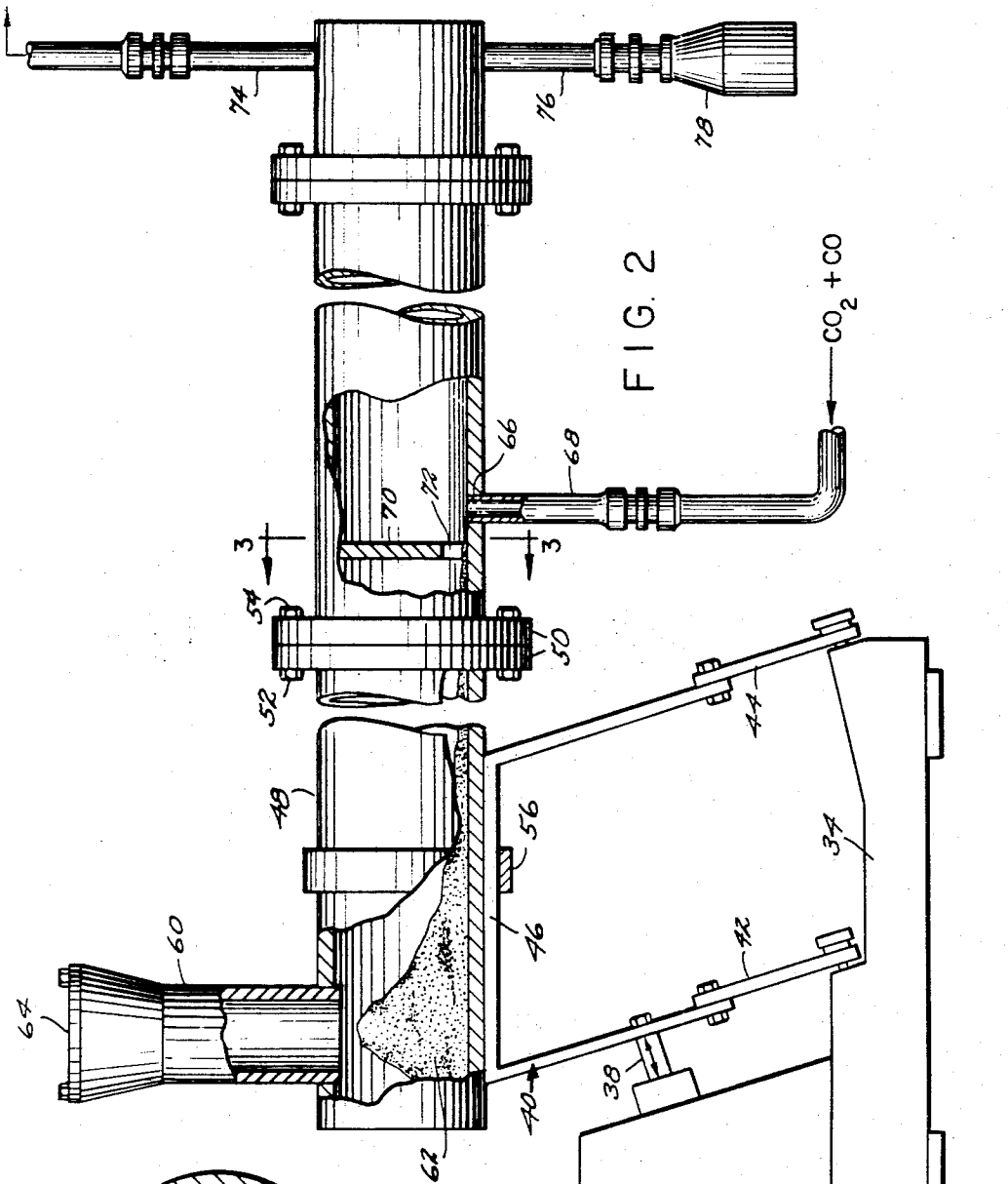


FIG. 2

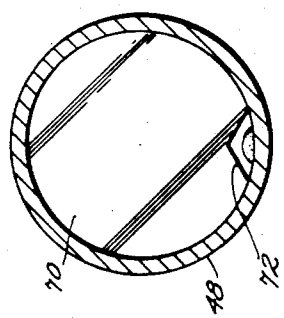


FIG. 3

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United States Patent Office 3,418,076
Patented Dec. 24, 1968

3,418,076

METHOD FOR CONTROLLING THE FEED OF NUCLEI IN THE PRODUCTION OF CRYSTALS BY VAPOR DEPOSITION

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Filed Apr. 14, 1965, Ser. No. 447,994
8 Claims. (Cl. 23—142)

ABSTRACT OF THE DISCLOSURE

An improved method of delivering solid nuclei to the reaction zone where single crystal whiskers are grown on the nuclei by deposition from the vapor phase. The nuclei are removed from a supply station and conveyed as a stream along a tube by mechanical vibrations which constantly agitate the nuclei and control the density of the stream. A carrier gas is injected into the stream at a point remote from the supply station to produce a mixture consisting of carrier gas and nuclei which is fed to the reaction zone.

This invention relates to the synthesis of single crystals and more particularly to improved process and apparatus for growing single crystals by vapor deposition.

It is well known that single crystals may be grown epitaxially on a substrate by deposition involving interaction of vapor phase reactants at the solid-vapor interface. Under controlled conditions of pressure, temperature, and supersaturation, it is possible to grow crystals in the form of fine fibers (also called "whiskers") characterized by high purity and crystalline perfection. Preferably, the single crystal fibers are grown on small nuclei of the same stoichiometric composition which are fed into the reaction zone at the same time as the vapor phase reactants. Although various compounds may be grown in whisker form, there has been considerable difficulty in doing so on a continuous or semi-continuous basis with consistency of results. While for the most part the inconsistency of results obtained by others is due to improper choice of reaction conditions, I have determined that it also is due in part to failure to feed the nuclei into the reaction zone at a substantially constant rate. In this connection, it is to be appreciated that precise control of supersaturation is essential in order to achieve proper growth and that precise control of supersaturation cannot be attained unless a steady reaction state exists in the reaction zone. However, steady state operation is determined by the equilibrium equation:

$$K_p = P_P / P_R$$

where P_P=partial pressure of the product gases and P_R= partial pressure of the reactant gases. The nuclei have a partial pressure with evaporation occurring at their surfaces. If the rate of nuclei delivery to the reaction zone varies, the rate of nuclei evaporation and the pressures in the growth region also will vary, thereby affecting the equation so as to drive the reaction in the forward or reverse direction according to the nature of the pressure change. Depending upon the extent of the change in rate of nuclei delivery, the affect on deposition from the vapor phase may vary from a mere change in crystal growth velocity to a change in growth form, e.g., a powder. Of course, this effect also will vary in degree with different crystal compositions. The desired control over rate of nuclei delivery is not easily achieved. For example, I have determined that it is not satisfactory to deliver nuclei from a fluidized bed or via conventional aspirator-type injectors. A fluidized bed comprising particles of a size suitable for the process tends to pulse and the rate of removal of nuclei from the bed to the reaction zone is not steady but instead is modulated more or less in accordance with the pulsing of the bed. Conventional aspirator-type injectors are not satisfactory because of cost as well as inadequate flow control.

Accordingly, the primary object of my present invention is to provide an improved method of growing single crystal fibers involving a novel mode of delivering nuclei to the crystal growth region at a controlled rate.

A more particular object of the invention is to provide an improved method of delivering selected nuclei to a reaction zone where single crystal fibers are grown on said nuclei by deposition from the vapor phase.

Another particular object is to provide novel apparatus for delivering nuclei to a reaction zone where single crystals are grown thereon by deposition from the vapor phase.

A further object of the invention is to produce crystal fibers of high purity and perfection at controlled growth rate.

Other objects and many of the attendant advantages of my invention will become more readily apparent as reference is had to the following detailed specification when considered together with the acompanying drawings wherein:

FIG. 1 schematically illustrates a preferred system for growing sapphire whiskers in accordance with the present invention;

FIG. 2 shows a preferred form of nuclei feeder embodying the present invention; and

FIG. 3 is a cross-sectional view taken along line 3—3 of FIG. 2.

The invention is described in detail hereinafter as applied to the production of sapphire whiskers. However, such description is intended to be merely illustrative and it is to be understood that the principles of my process and apparatus are applicable to the production of crystals of different composition.

The system shown in FIG. 1 is adapted to accomplish vapor phase growth of sapphire whiskers according to a preferred process based upon the following reaction equation:

$$2AlCl_3(g)+7H_2(g)+CO(g)+3CO_2(g)+4Cl_2(g) \leftrightharpoons Al_2O_3(s)+4CO(g)+14HCl(g)$$

The system comprises a reaction chamber in the form of a closed furnace **2** which is heated by suitable means such as an electric resistance coil **4**. At its inlet end, the furnace is connected to an inlet line **6** that is fed by two supply lines **8** and **10**. The former leads to a source **12** of highest purity aluminum chloride ($AlCl_3$) gas and separate sources **16** and **18** of highly pure chlorine and hydrogen. Line **10** leads to a source **20** of nuclei and separate sources **22** and **24** of highly pure carbon dioxide and carbon monoxide. The nuclei consists of α-alumina particles whose size is in the order of microns. The nuclei and CO_2—CO mixture are brought together by means of the apparatus of FIG. 2, whereupon the nuclei become entrained in the gas mixture and are delivered by the latter to the furnace. Although not shown, it is to be understood that control valves, flow meters, and pressure gauges are provided at appropriate points to permit individual regulation of the flow of each of the five gases $AlCl_3$, Cl_2, H_2, CO, and CO_2). Electrical resistance heating coils such as coil **26** are provided to preheat the gases before they enter the furnace.

At its downstream end, the furnace has an outlet line **28** which is connected via a crystal separator **30** to a vacuum pump **32**. The latter is adapted to withdraw gases

and whiskers from the furnace while maintaining the overall reaction chamber pressure at a desired level. Crystal separator **30** is essentially a filtering device adapted to pass the gaseous effluent from the reaction chamber while retaining the whisker-bearing nuclei.

The temperature within the furnace is kept constant at a selected level at which whisker growth will occur according to the foregoing overall reaction equation under given flow and pressure conditions. Thermocouples (not shown) may be used to determine the temperature within the furnace as well as the temperature of the gases as they enter the reaction chamber. Suitable means (also not shown) are employed to monitor the pressure within the furnace at all times during whisker production.

Turning now to FIG. 2, the apparatus for achieving controlled delivery of nuclei to the reaction chamber comprises a base **34** supporting an electrically powered vibrator unit **36** that is of conventional design and has an output shaft **38** that reciprocates at a suitable frequency, e.g., 600 cycles per second. Although not shown, it is to be understood that the vibrator unit includes means for adjusting its output amplitude, i.e., the length of the stroke of shaft **38**. Attached to the base in inverted position is a generally U-shaped support member **40** consisting of a pair of inclined legs **42** and **44** connected at one end by an intermediate horizontal bar **46**. Shaft **38** is connected to leg **42**. The two legs **42** and **44** are relatively stiff and have just enough resiliency to flex in response to reciprocal movement of shaft **38**. As a consequence of the geometry of the foregoing arrangement, the intermediate bar **46** will oscillate along a path of movement characterized by a relatively large horizontal vector and a relatively small vertical vector, i.e., at an acute angle to the plane of bar **46**.

Mounted on bar **46** of support member **40** is an assembly comprising an elongated housing in the form of a tube **48** which preferably is made up of several sections that are releasably secured together in a suitable manner. By way of example, the illustrated embodiment comprises three sections having mating flanges **50** that are secured together by a plurality of bolts **52** and nuts **54**. This arrangement facilitates disassembly for inspection and cleaning purposes. The tube may be secured to the U-shaped support member in any conventional manner, such as by one or more friction bands **56** or by welding or cementing. The exact manner in which tube **48** and its vibratory support member **40** are united is not critical except that the two members must vibrate as one assembly. It also is preferred that the connection between support member **40** and tube **48** be at or adjacent to one end of the tube as shown.

Both ends of tube **48** are closed by end walls. However, at the end that is attached to support member **40**, the top side of tube **48** is provided with a relatively large inlet hole in which is mounted an upstanding tubular chute **60** for introduction of nuclei **62**. The chute is provided with a removable cover **64**. At a suitable point downstream of chute **60**, the tube **48** has another inlet hole **66** fitted with a pipe **68** for admittance of a carrier gas. In the illustrated embodiment, pipe **68** is connected to the CO_2 and CO gas sources **22** and **24** respectively. Inlet **66** is located on the underside of tube **48** at the six o'clock position. Mounted within tube **48** intermediate chute **60** and inlet **66** is a baffle plate **70** provided with an opening **72** of suitable size at the six o'clock position. Preferably, the baffle plate is located close to inlet **66** as shown.

At its opposite end, the tube **48** is fitted with two outlet pipes **74** and **76** located at the twelve and six o'clock positions, respectively. Pipe **74** leads to the furnace **2** and corresponds to line **10** in FIG. 1. Pipe **76** carries a removable container **78** at its bottom end.

Operation of the apparatus of FIG. 2 will be readily understood from the following example illustrating how α-alumina whiskers may be grown with and according to the present invention:

Example

Chute **60** is filled with a charge of alumina nuclei having a size in the range of 5–10 microns, and cover **64** is secured in place. Furnace **2** is heated to about 1560° C. and the gas supply lines are heated to a level such that the various gases will be at a temperature of 300–400° C. as they enter the reaction chamber provided by furnace **2**. At the same time, the system is pumped down to a vacuum of about 50 microns of mercury. Then vibrator unit **36** is started and gas flow is initiated with hydrogen flow commencing last. The flow rates of the various gases in liters per minute are as follows: aluminum chloride—0.03; hydrogen—0.95; chlorine—0.02; carbon dioxide—0.80; and CO—0.22. Thereafter, the pressure within the reaction chamber is adjusted to 5.5 mm. of mercury and is maintained at that level during the run. The foregoing flow rates and temperatures also are held constant during the run.

Under the influence of vibrator unit **36** acting through shaft **38** and support member **40**, tube **48** will oscillate steadily in a generally longitudinal direction. This vibratory movement causes the alumina nuclei to migrate away from the stockpile at chute **60** toward baffle plate **70**. The migrating nuclei form a continuous stream in which each particle is constantly agitated. The stream rapidly shrinks in width as it moves away from the stockpile. This shrinkage in width is due at least in part to the geometry of tube **48**, the particles tending to assume the six o'clock position in the tube. The density of the stream is controlled by the operating level of the vibrator unit. The stream is at its minimum width and has a substantially constant density by the time it reaches and passes through the hole **72** in baffle plate **70**. The latter prevents turbulent backflow of the CO_2–CO gas mixture toward chute **60** and thus prevents any substantial disturbance of the nuclei stream until after it passes through hole **72**. As the nuclei move past the baffle plate, they are swept up by and become suspended in the incoming stream of CO_2–CO gas mixture. The nuclei are swept up as fast as they move downstream of the baffle plate so that the concentration thereof in the CO_2–CO gas delivered to furnace **2** remains constant during the run.

Under the foregoing operating conditions, alumina whiskers form on the nuclei in furnace **2**. These whisker-bearing nuclei are collected in the crystal separator during the run which is terminated after the supply of nuclei has been consumed. Little growth occurs on the furnace walls, and the lines leading to and from the furnace are clean and free of crystal growth. The product recovered from crystal separator **30** consists of rhombohedral, prismatic, and hexagonal alpha-alumina whiskers grown on the injected nuclei. The whiskers have lengths up to ¾ inch and diameters in the order of about 7 microns. Their tensile strength measured at room temperature is in the range of 1.8 to 2 million pounds per square inch.

The results achieved according to the foregoing example are typical and can be reproduced repetitively using the novel apparatus of FIG. 2. It has not been possible to achieve comparable consistency of results when delivering nuclei in accordance with prior art practices, e.g., from a fluidized bed or by means of conventional aspirator-type injection nozzle. Unlike prior art equipment, the rate of introduction of nuclei is not controlled wholly by the rate of flow of the carrier gas (i.e., the CO_2—CO mixture in the foregoing example), but is variable according to the level of operation of the vibrator unit. Thus, within certain limits, the rate of delivery of nuclei can be adjusted without modifying the rate of flow of the carrier gas. A further advantage resides in the fact that the carrier for the nuclei can be one or a mixture of the gases involved in the reaction (as in the foregoing example) or may be an inert gas such as argon. Another advantage is that nuclei that are too large to be swept out of tube **48** by the carrier gas cannot collect at a flow obstructing point but

instead drop via pipe **76** into container **78** from which they can be removed at a convenient time.

Of course, the apparatus of FIG. 2 is applicable to the growth of whisker-form crystals of other substances, e.g., boron, which can be formed on nuclei by deposition from a vapor phase reaction. The manner in which the equipment is constructed and its mode of operation allows continuous operation without need for frequent interruptions to clean out lines, nozzles, etc.

It is to be understood also that the cross-sectional shape of the tube **48** need not be circular as shown but may conform to any other suitable configuration which tends to promote formation under the influence of gravity of a narrow stream of nuclei along its bottom side. Thus, tube **48** could have a triangular shape with its side walls converging at the bottom and the carrier gas inlet pipe **68** mounted close to the bottom edge of either side or else partially in both sides. Accordingly, it is to be understood that use of the terms "underside" or "bottom side" in connection with location of the nuclei stream in tube **48** (whether of circular or other suitable configuration) is intended to denote the low point in the tube, e.g., the six o'clock position shown in FIG. 3. It is to be noted also that best results are obtained if the diameter of pipe **68** is such that the carrier gas stream has a width comparable to the stream of nuclei so as to assure that it is uniformly affected by the carrier gas.

Of course, the invention is not limited in its application to the details, arrangement, or example specifically described or illustrated, and within the scope of the appended claims, it may be practiced otherwise than as specifically described or illustrated.

I claim:

1. In a process for growing crystals on selected nuclei by deposition from a vapor phase reaction involving a plurality of selected reactants occurring in a reaction chamber, the improvement consisting of establishing a supply of solid nuclei whose size is in the order of microns, removing nuclei from said supply and conveying said removed nuclei as a thin constantly agitated stream along an elongate tube by mechanically vibrating said tube, injecting a carrier gas into said stream as it advances along said tube so as to remove nuclei therefrom and produce a mixture consisting of nuclei suspended in said carrier gas, and delivering said mixture to said reaction chamber.

2. A process as defined by claim **1** wherein said carrier gas is one of said selected reactants.

3. The method of claim **1** wherein said carrier gas is injected as a stream which is at least as wide as said stream of nuclei.

4. The method of claim **1** wherein said tube is substantially horizontal and said carrier gas is injected into the bottom side of said tube.

5. A process as defined by claim **1** wherein said vapor phase reaction produces Al_2O_3 crystals and said reactants comprise $AlCl_3$, Cl_2, H_2, CO_2 and CO.

6. A process as defined by claim **5** wherein said nuclei are particles of alumina.

7. In a process for growing alumina crystals on selected solid nuclei by deposition from a vapor phase reaction occurring in a reaction chamber, the improvement consisting of establishing a supply of solid nuclei with a particle size in the order of microns adjacent one end of an elongate tube which extends in a generally horizontal direction, subjecting said tube to mechanical vibrations so as to cause said nuclei to migrate away from said supply toward the opposite end of said tube in a thin free-flowing stream that is confined by gravity to the bottom side of said tube and moves at a substantially constant rate, injecting a carrier gas into said stream via an opening in the bottom side of said tube at a velocity sufficient to remove nuclei from said stream and form a mixture consisting of nuclei suspended in said gas, and delivering said mixture to said reaction chamber at a controlled rate.

8. The invention of claim **7** wherein said vapor phase reaction involves $AlCl_3$, Cl_2, H_2, CO_2 and CO gases with at least one of said gases serving as the carrier for said nuclei.

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U.S. Cl. X.R.

23—209, 273, 1; 302—33, 42