May 23, 1972 E. F. HOLLANDER, JR 3,664,813

METHOD FOR MAKING GRAPHITE WHISKERS

Filed July 17, 1969 4 Sheets-Sheet 1

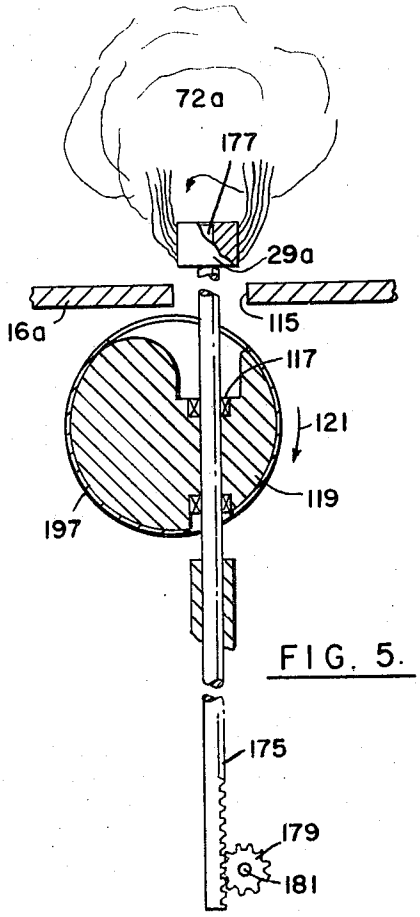


FIG. 5.

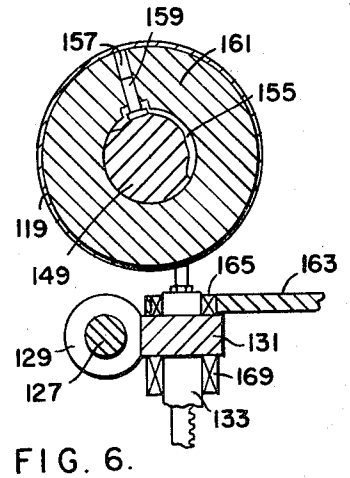


FIG. 6.

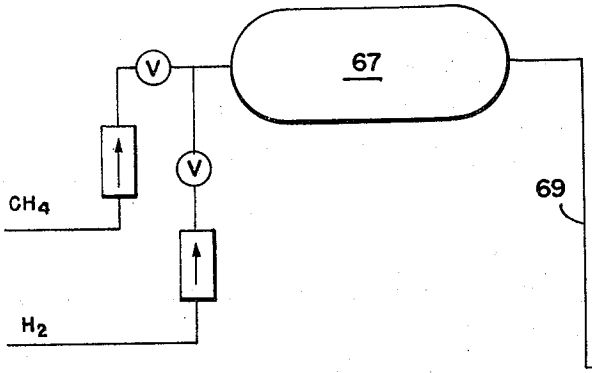
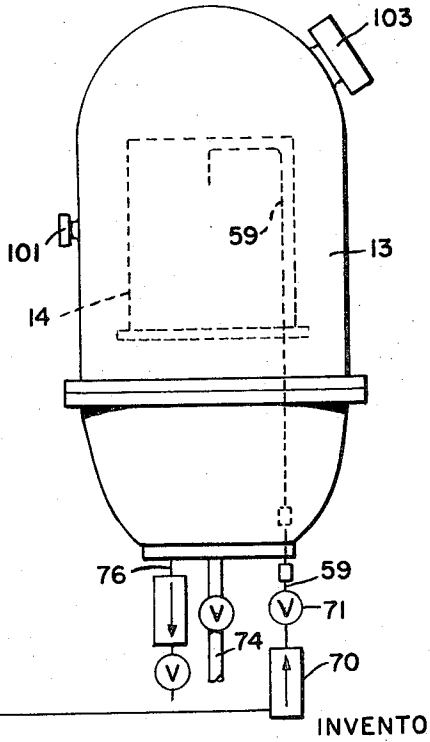


FIG. 1.



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METHOD FOR MAKING GRAPHITE WHISKERS

Filed July 17, 1969 4 Sheets-Sheet 2

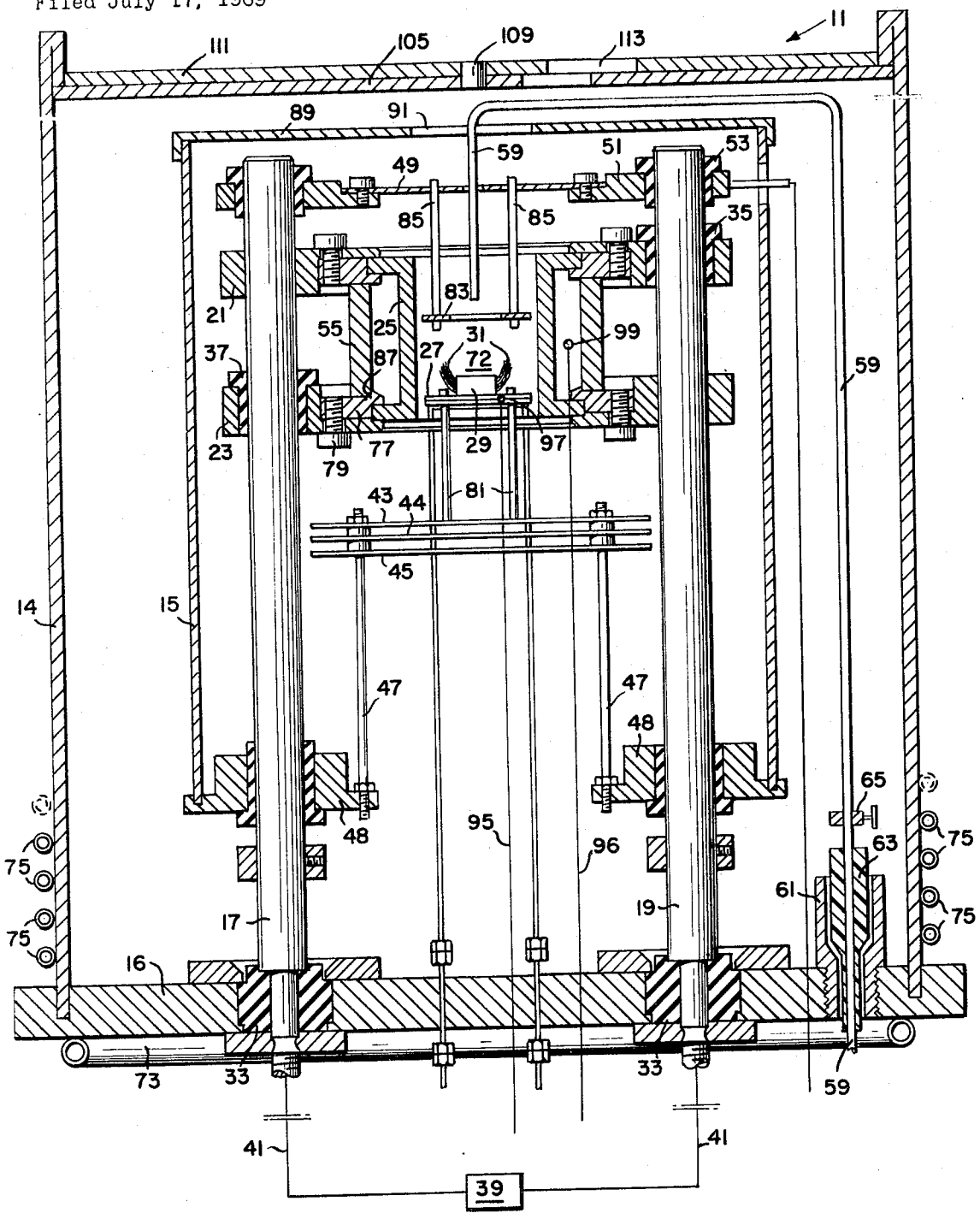


FIG. 2.

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METHOD FOR MAKING GRAPHITE WHISKERS

Filed July 17, 1969 4 Sheets-Sheet 3

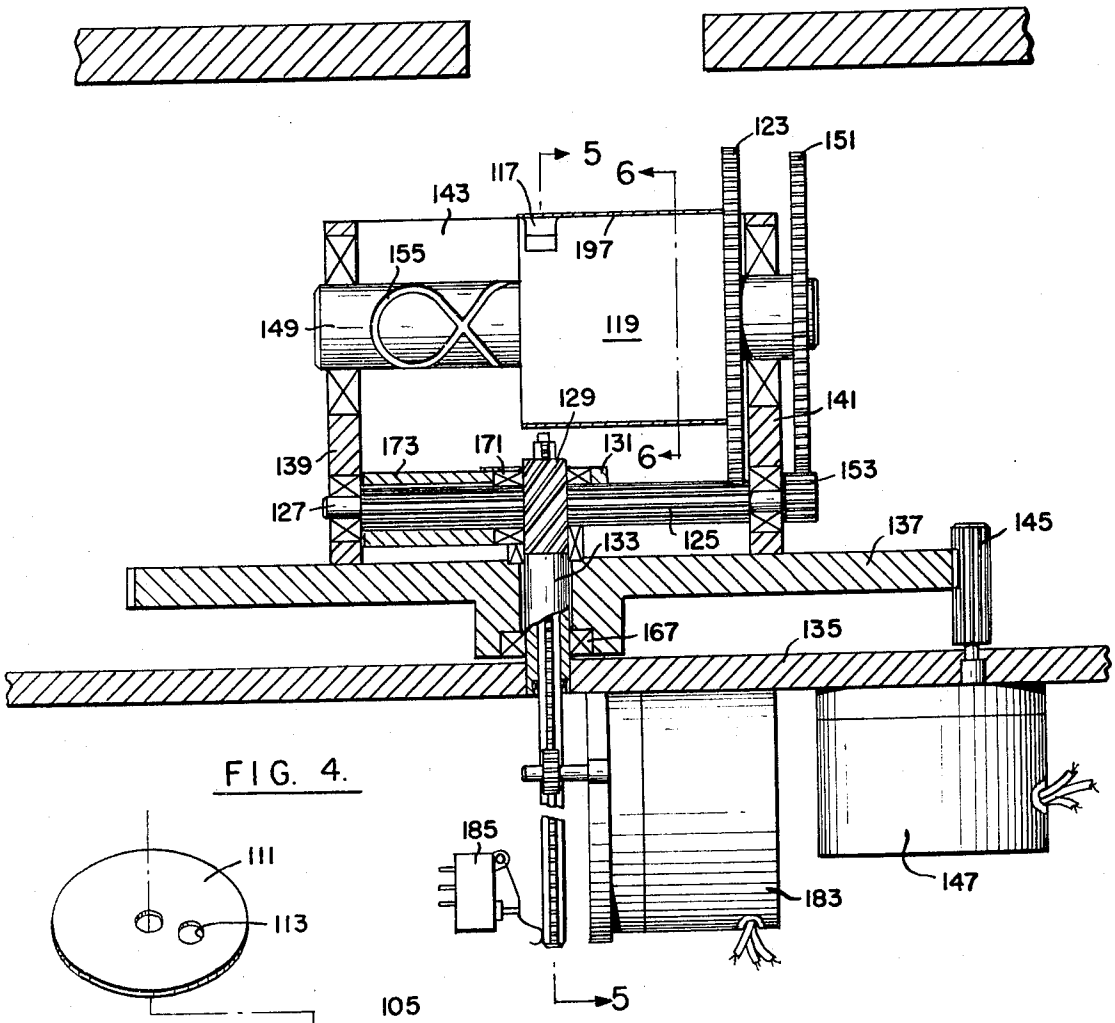


FIG. 4.

FIG. 3.

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METHOD FOR MAKING GRAPHITE WHISKERS

Filed July 17, 1969 4 Sheets-Sheet 4

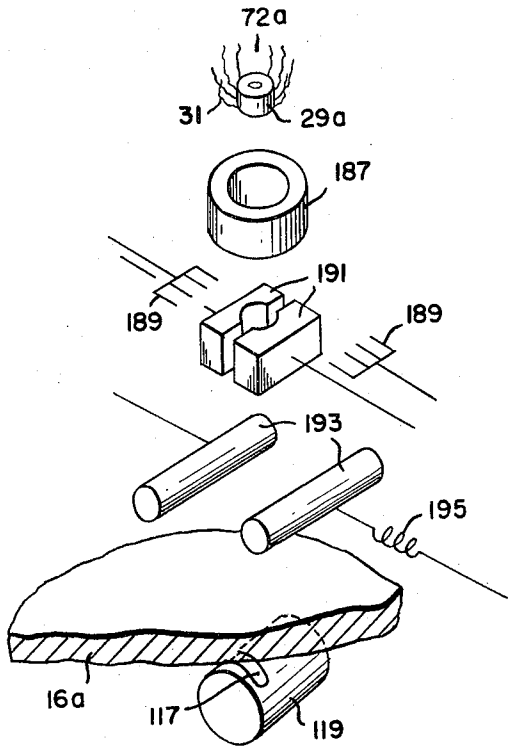


FIG. 7.

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3,664,813

METHOD FOR MAKING GRAPHITE WHISKERS

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Int. Cl. C01b 31/04, 31/07
U.S. Cl. 23—209.1 9 Claims

ABSTRACT OF THE DISCLOSURE

An oven for making whiskers from a vapor comprising a housing containing a chilled base plate, a first and second support post extending upwardly from the base plate, an upper and lower support plate mounted on the posts, a hollow heating element mounted between the support plates, and a stage within the heating element for supporting a substrate on which whiskers are grown. The substrate is covered with rhodium, and may be made of a material selected from the group consisting of stainless steel, beryllium oxide, alumina, copper, cobalt, and nickel. The method includes placing a substrate in a whisker deposition zone of whisker vapor, and depositing and growing whiskers on the substrate. The method also includes cooling the bottom of the whisker deposition zone to form convection currents of vapor passing upwardly through the zone, and feeding the vapor downwardly into the whisker deposition zone to clash with the upwardly flowing vapor convection currents and form a turbulence in the whisker deposition zone. A rotatable drum positioned below a nucleating zone in the oven and having a pocket that receives the substrate. A rack gear operated by a motor with a clutch moves the substrate from the nucleating zone to the drum pocket, and a motor gear system rotates the drum to wind the whiskers in the form of a roving onto the drum so that courses of a succeeding layer of roving lie between courses of the next preceeding layer having courses running in the same direction.

BACKGROUND OF THE INVENTION

This invention relates to a method and an oven for making fibers or whiskers by condensing material from a vapor phase, and a drum for winding the whiskers into a coil in the form of a roving.

It has long been known that crystal structures are very much stronger than the same material in non-crystalline form. Accordingly, it has been desired to produce crystalline material having long, needle-like linear crystals, commonly referred to in the art as crystalline fibers or whiskers. Much work is being done to develop a reliable method and apparatus for producing whiskers, such as graphite whiskers.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method and apparatus for producing whiskers reliably and consistently, and for winding the whiskers into a coil. This involves providing an oven including a chilled base plate and a hollow heating element mounted above the base plate with a stage positioned within the heating element for supporting a substrate on which the whiskers are grown. The substrate may be made of a number of materials, and it has been found that when the substrate is covered with rhodium that whiskers are produced at a greatly accelerated rate. Also, it has been found beneficial to create convection currents of vapor in the oven which flow upwardly through the heating element, and to direct the feed vapor downwardly through the heating element to form a turbulent deposition zone within the heating element. It also involves providing a drum and means for winding the whiskers on the drum in the form of a roving.

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and advantages of this invention, including its simplicity and economy, as well as the ease with which it may be adapted to existing equipment, will further become apparent hereinafter and in the drawings, in which:

FIG. 1 is a view, partly schematic, of whisker oven apparatus constructed in accordance with this invention;

FIG. 2 is view in vertical section of the oven of FIG. 1;

FIG. 3 is a perspective and exploded view of an outer heat shield housing forming part of the oven;

FIG. 4 is a view partly in section of the winding apparatus of this invention;

FIG. 5 is a view in section taken as indicated by the lines and arrows 5—5 which appear in FIG. 4;

FIG. 6 is a view in section taken as indicated by the lines and arrows 6—6 which appear in FIG. 4; and

FIG. 7 is an exploded view in schematic form of feed structure located between nucleation zone and the drum of the winding apparatus.

Although specific terms are used in the following description for clarity, these terms are intended to refer only to the structure shown in the drawings, and are not intended to define or limit the scope of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Turning now to the specific embodiment of the invention selected for illustration in the drawings, there is shown a whisker oven **11** comprising a housing **13**, an outer heat-shield **14**, an inner heat-shield **15** containing a chilled base plate **16**, a first support post **17** and a second support post **19** extending upwardly from base plate **16**, an upper annular support plate **21** and a lower annular support plate **23** mounted on posts **17** and **19**, a hollow graphite heating element **25** mounted between support plates **21** and **23**, and a chilled stage **27** mounted within heating element **25** for supporting a substrate **29** on which whiskers **31** are grown.

Oven **11** includes electrical insulators **33** positioned between the posts **17**, **19** and base plate **16**. An electrical insulator **35** is positioned between support post **19** and upper support plate **21**, and electrical insulator **37** is positioned between support post **17** and lower support plate **23**. A source of electric current **39** is connected by electrical conductors **41** to support posts **17**, **19**, so that current flows through post **19**, lower support plate **23**, heating element **25**, upper support plate **21**, and downwardly through support post **17** to return to current source **39** to thereby heat the heating element **25**.

Three molybdenum discs **43–45** are supported from posts **17**, **19** by rods **47** and ring **48** and are positioned below heating element **25** to prevent excessive heat loss downwardly.

Above heating element **25**, a molybdenum disc **49** is supported from posts **17**, **19** by annular plate **51** and forms a heat shield for preventing excessive heat loss upwardly. Electrical insulators **53** are positioned between plate **51** and posts **17**, **19** to prevent electrical current flow from posts **17**, **19** to plate **51**.

A hollow cylinder **55** of fused quartz is supported between plates **21** and **23** and is positioned around heating element **25** for preventing excessive heat loss outwardly.

A gas or vapor, such as methane or natural gas, is fed into oven **11** from a vapor source through a tube **59** encased in a stainless steel sleeve **61** threaded into base plate **16** and having a plastic insert **63** positioned between tube **59** and sleeve **61** to electrically insulate the

tube 59 from base plate 16. Insert 63 is preferably made of Teflon, and a tube clamp 65 is provided for adjusting the vertical position of tube 59, since normally clamp 65 abuts the top of insert 63.

Apparatus is provided for varying the pressure in oven 11, and this apparatus includes a tank 67 (FIG. 1) connected to oven 11 by conduit 69, flowmeter 70, valve 71, and tube 59. Argon and methane, or hydrogen and methane are mixed together in a mixing vessel or tank 67 which is similar in construction to oven 11, and the mixture of gases is fed into the interior of oven 11 until the desired pressure is reached. Satisfactory results in growing whiskers have been obtained at one atmosphere, but operation at about 4 or 5 atmospheres is preferred. In any event, the pressure within oven 11 must be positive, since no deposition of whiskers has been obtained at negative pressures.

Vacuum line 74, sufficient to exhaust the furnace to 10–4 torr, is provided for scavenging undesired vapors and gases, such as oxygen, from the furnace before beginning nucleation and growth of the crystal whiskers. Exhaust line 76 is provided for controlling the pressure in the furnace and for exhausting the unwanted decomposition products of the reaction, such as hydrogen in the case of methane.

While whisker deposition has been obtained using substrates made of a variety of materials, it has been found that when the substrate is made of some other materials there is no whisker deposition. For example, whisker deposition has been obtained when the substrate has been made of 300 series stainless steel without selenium or sulfur or similar agents used for free machining, beryllium oxide, alumina, copper, cobalt and nickel. Moreover, greatly accelerated graphite whisker deposition was obtained when the substrate was coated with rhodium. The rhodium appears to act as a catalyst and produces a fibrous, woolly, cotton-ball material which may be used to reinforce rubber, for example. The use of rhodium increased the nucleation and growth of the whiskers about ten thousand times.

Not all materials may be used as a substrate. For example, tests have shown that the following materials do not work as a substrate to produce graphite whisker deposition and growth: silica, aluminum, tungsten, molybdenum, gold, and silver.

The temperature of heating element 25 may be varied by varying the output of the electrical current source 39. For graphite whisker nucleation and growth to occur at all, a specific thermal gradient is important and also the absolute temperature of the substrate is important. Moreover, the temperature must stay fixed and not wander. For example, the substrate temperature may be 1150° F. or 1250° F., but whichever temperature is chosen, the substrate should stay within about 1° F. of that chosen temperature.

Gas tube 59 extends upwardly and then curves downwardly to feed the gas downwardly into a whisker nucleating or deposition zone 72 around substrate 29 and form a turbulence with vapor convection currents created by the coolness of chilled base plate 16.

Base plate is cooled by a cooling tube 73 and outer heat shield 14 is cooled by cooling tubes 75.

Heating element 25 is supported on plate 23 by split ring clamps 77 and bolts 79, and stage 27 is supported by rods 81 that extend upwardly from disc 43.

An annular molybdenum disc 83 is positioned within heating element 25 above stage 27 and is supported by rods 85 that extend downwardly from molybdenum disc 49.

Fused quartz cylinder 55 is held reasonably concentric to heating element 25 by a shoulder 87 on clamping ring 77.

Inner heat-shield 15 is preferably made of molybdenum, and is provided with an annular cover 89 having a hole 91 through which tube 59 projects downwardly toward nucleating zone 72.

Electrical conductors 95, 96 pass through the bottom of housing 13 and lead, respectively, to thermocouple 97 bolted to the bottom of stage 27 and to thermocouple 99 positioned between heating element 25 and quartz cylinder 55.

Whisker oven housing 13 is a split tank and is provided with vacuum and pressure gauges, side windows 101 for looking into the interior, and a larger window 103 at the top.

Outer heat-shield 14 is provided with a top wall 105 having three sight holes 106–108 of various sizes and a bearing 109 on which a top plate 111 is rotatable. Plate 111 has a sight hole 113 that may be positioned over any of sight holes 106–108 as desired so as to watch the nucleation in zone 72.

Substrate 29 is cylindrical in shape and the whiskers 31 grow on the outer surface of the cylinder. However substrates of different shapes may be used.

In practice, it has been noted that if there are too many vapor atoms in the oven trying to deposit on the substrate 29, proper nucleation does not occur. On the other hand, I have achieved nucleation, following careful purging of the oven by pumping the vacuum chamber to about 1/10 micron, refillling the chamber with a clean inert gas such as argon and repeating these steps three times until the level of contamination is low, by setting the proper thermal gradient in the oven by heating the element 25 to about 1450° F. with the pressure in the oven 11 being a negative pressure, i.e. a vacuum. Then I flooded the oven 11 with natural gas containing methane until the pressure rose above fifteen millimeters of mercury to start deposition of whiskers. Then I dropped the temperature of the heating element 25 to about 1200° F. and the growth of whiskers continued.

Chilled base plate 16 serves a dual purpose in that it protects the instruments below plate 16 from heat, and also promotes convection of vapor current in the oven to thereby stimulate and promote the growth of whiskers.

A temperature gradient exists between heating element 25 and substrate 29. Similarly, a tempearture gradient exists between heating element 25 and the whisker growth ends 31. Satisfactory growth has been achieved when these gradients were between 300° F. per inch and 1200° F. per inch. This is a function of the geometry of the furnace.

The method of the present invention comprises placing a substrate 29 in a whisker deposition zone 72 of whisker vapor by placing substrate 29 on stage 27, and depositing and growing whiskers on the substrate 27. The substrate is made of a material selected from the group consisting of rhodium, stainless steel, beryllium oxide, alumina, copper, cobalt and nickel, and excellent results have been obtained from a beryllium oxide substrate coated with rhodium. Graphite whiskers have been grown using methane as the vapor, and also when using neutral gas containing a high percentage of methane.

The temperature of the whisker vapor has been maintained in the deposition zone at about 1200° F., and whisker deposition has been obtained with the pressure at fifteen millimeters of mercury, one atmosphere, and up. However, no whiskers were obtained when the pressure in the oven has been negative.

The method also includes the steps of cooling the bottom of the whisker deposition zone by chilling plate 16 to form convection currents of vapor that pass upwardly through the vapor deposition zone, and feeding the vapor downwardly from tube 59 into the whisker deposition zone to clash with the upwardly flowing vapor convection currents and form a turbulence in the vapor deposition zone around the substrate 29.

Referring now more particularly to FIGS. 3–7, there is shown winding apparatus which may be incorporated

in the whisker oven and positioned below a nucleating zone **72***a* that corresponds to nucleating zone **72** in FIG. 2. A base plate **16***a* corresponds to base plate **16** in FIG. 2. Most of the apparatus in FIG. 2, is duplicated in FIG. 5 but has been omitted for clarity. However, some of the structure of FIG. 2, the supporting structure lying between the nucleating zone **72** and base plate **16**, is left out entirely because substrate **29***a* is adapted for movement downwardly from nucleating zone **72***a* through a hole **115** in plate **16***a* to seat in a pocket **117** formed in a drum **119** rotatable in the direction of arrow **121**.

The winding apparatus includes drum **119** having a gear **123** that rotated by an elongated gear **125** mounted on a shaft **127**. A left-hand helical gear **129** is also mounted on shaft **127** and is caused to rotate when shaft **127** moves around a fixed left-hand helical gear **131** supported in fixed position by stationary shaft **133** that extends upwardly from fixed plate **135**.

Shaft **127** is caused to move around fixed gear **131** by the rotation of gear **137** on which is mounted end plates **139, 141**. Shaft **127** is mounted supported at its ends in plates **139, 141**. A third end plate **143** connects one end of plate **139** to an end of plate **141** to form a strong three-sided box structure of plates **139, 141** and **143**.

Gear **137** is caused to rotate by a pinion **145** mounted on the shaft of motor **147**.

Drum shaft **149** is mounted between end plates **139** and **141** and is positioned interiorly of drum **119**. A gear **151** is mounted on the end of shaft **149** and is driven by a pinion **153** of shaft **127**. Pinion **153** has a slightly larger pitch diameter than elongated gear or pinion **125**. Shaft **149** is provided with a cam groove **155**, and drum **119** is provided with a hole **157** in which is positioned a spring-loaded stem **159** having a shoe **161** that rides in groove **155** to give axial movement to drum **119**. The teeth of pinion **153** have a slightly larger pitch diameter than the teeth of pinion **125** so that the speed of the axial movement of drum **119** is slightly different than that dictated by revolutions of pinion **125** and gear **123** alone. Accordingly, courses of a succeeding layer of roving lie between courses of the next preceeding layer having courses running in the same direction.

A support plate **163** is provided for supporting a bearing **165**, and a bearing **167** is mounted in gear **137**. Bearings **165** and **167** serve as bearings about which the entire frame assembly including gear **137** and end plates **139, 141** and **143** rotate. A bearing **169** supports gear **131**, and a bearing **171** and support sleeve **173** support helical gear **129**.

To raise and lower substrate **29***a*, a gear rack **175** is provided having a reduced end portion **177** which is received by a hole in the bottom of substrate **29***a*. Gear rack **175** is driven by a driving gear **179** mounted on shaft **181** of motor **183** having an electrically operated clutch on its shaft **181**. When rack gear **175** is moved downwardly to deposit substrate **29***a* in pocket **117**, switch **185** is activated to open the clutch on motor **183** thereby allowing rack gear **175** to drop quickly by gravity to a position clear of drum **119** as shown in FIG. 4. This use of the clutch-motor is advantageous over using a complicated and expensive two speed motor.

FIG. 7 is an exploded view in schematic form of the feed structure of the invention located between nucleating zone **29***a* and chilled base plate **16***a*. A ring **187**, preferably of alumina, forms a funnel guide for whiskers **31** to aid in restricting the movement of the whiskers outside nucleating zone **29***a*. A pair of forks **189**, shown separated, are brought together by a solenoid acting upon a signal from switch **185**. The forks **189** hold the whiskers **31** as they pass through the forks and prevent the growth ends from turning as the roving is twisted below. A pair of split guides **191** are also brought together by a solenoid upon a signal from switch **185** and in closed position, the guides **191** form a circular or cylindrical hole through

which whiskers **31** pass and are supported in an upright position. Guides **191** support the weight of the long roving and add some tension to the roving as it winds onto the drum **119**.

A pair of tension rolls **193** are positioned beneath guides **191** and are spring loaded by spring **195**. Rolls **193** are brought together by a solenoid that is actuated by switch **185** and they apply tension to the roving to aid in the winding of the roving onto drum **119**. Rolls **193** and guides **191** are preferably made of alumina, and forks **189** are preferably made of **310** stainless steel.

Drum **119** is provided with a self-supporting cone **197** which is shown in section in FIG. 4 and which slips on and off drum **119** to form the core of the round roving. To mount cone **197** on drum **119**, the operator pulls out shaft **149** from its bearings in end plates **139** and **141**, and then cone **197** is slipped over drum **119**. To remove cone **197** from drum **119** when the cone has been wound with whiskers, the reverse procedure is followed: shaft **149** is pulled out of its bearings and the cone **197** is pulled off drum **119**.

In operation of the winding apparatus shown in FIGS. 3 to 7, substrate **29***a* is moved upwardly into nucleating zone **72***a* by rack gear **175** and nucleation is started. As nucleation progresses and the whiskers **31** grow, substrate **29***a* is moved downwardly by rack gear **175** at such a speed that the wisps of the whiskers **31**, the growing ends, remain in nucleating zone **72***a*. When the substrate **29***a* seats in pocket **117** of drum **119**, switch **185** actuates the clutch mechanism of motor **183** to release its clutch mechanism so that rack gear **175** drops very quickly by gravity through the hole in drum **119** to the position shown free of the drum in FIG. 4. Then motor **147** starts to rotate pinion **145** which rotates the entire assembly mounted on gear **137** including end plates **139, 141** and shafts **127** and **149**. The rotation of shaft **127** in a horizontal plane parallel to the plane of gear **137** causes rotation of shaft **127** as helical gear **129** moves around fixed helical gear **131**. Rotation of shaft **127** causes rotation of pinion **125** which rotates gear **123** and drum **119**. Rotation of shaft **127** also causes rotation of pinion **147** which rotates gear **151** and drum shaft **149** at a different rate of speed from the rotation of gear **123** and drum **119**.

With drum **119** rotating, the whisker roving is wound on drum **119** as the action of shoe **161** in groove **155** moves drum **119** back and forth longitudinally. Because pinion **153** rotates gear **151** at a different speed than that which pinion **155** rotates gear **123**, the courses of a succeeding layer of roving lie between the courses of the next preceding layer having courses running in the same direction.

The feed of the roving into the drum is controlled by ring **187**, forks **189**, guides **191** and tension rolls **193** positioned above the drum.

When the roving has been fully wound on drum **119**, the winding is removed by removing cone **197** from the drum in the manner herein before described. Then the cone is removed from the interior of the coil, and the strand of whiskers may be unwound from the coil by pulling from the inside or interior of the coil.

The entire apparatus may be used vertically inverted, and the resetting of the mechanism is simplified by using motors with clutches in their output shafts. The twist in the roving is preferably in the order of one twist per three inch length of roving, and the pull rate of the roving is preferably about four inches per hour or faster.

What is claimed is:

1. In a method of making graphite whiskers by depositing and growing whiskers on a substrate, the steps comprising covering the substrate with rhodium, placing the rhodium covered substrate in a whisker deposition zone of hydrocarbon whisker vapor, maintaining said zone at positive pressure at about 1150–1450° F., provid-

ing a temperature gradient around said substrate by chilling said substrate and depositing and growing whiskers on the rhodium covered substrate.

2. In a method of making graphite whiskers by depositing and growing whiskers on a substrate, the steps comprising providing a substrate made of a material selected from the group consisting of rhodium, 300 series stainless steel, beryllium oxide, alumina, copper, cobalt, and nickel, placing the substrate in a whisker deposition zone of hydrocarbon whisker vapor, maintaining said zone at about 1150–1450° F., providing a temperature gradient around said substrate by chilling said substrate, and depositing growing whiskers on the substrate.

3. The method of claim 2, including holding the temperature of the substrate in the deposition zone steady at a desired temperature.

4. The method of claim 2, wherein the whisker vapor is methane.

5. The method of claim 2, wherein the whisker vapor is natural gas.

6. The method of claim 2, wherein the whisker vapor is an aromatic hydrocarbon.

7. The method of claim 2, wherein the pressure in the whisker deposition zone is in the range of about 1–5 atmospheres.

8. The method of claim 2, including cooling the bottom of the whisker deposition zone to form convection currents of vapor passing upwardly through the zone.

9. The method of claim 8, including feeding the vapor downwardly into the whisker deposition zone to clash with upwardly flowing vapor convection currents and from a turbulence in said zone.

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U.S. Cl. X.R.

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