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(54) **METHOD FOR MANUFACTURING PITCH-BASED CARBON FIBER**

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(57) **ABSTRACT**

The present invention provides a method for manufacturing pitch-based carbon fiber by melt-spinning a mesophase pitch having optical anisotropy by using nozzles each equipped with an introduction hole entry portion, an introduction hole, an approach portion, and a discharge hole, and then applying thereto infusibilization, carbonization, or graphitization, wherein the mesophase pitch is passed through a plurality of contraction holes disposed in a substantially straight line in the introduction hole entry portion of each nozzle, then expanded in the introduction hole, and thereafter contracted in the approach portion and then spun by being passed through the discharge hole.

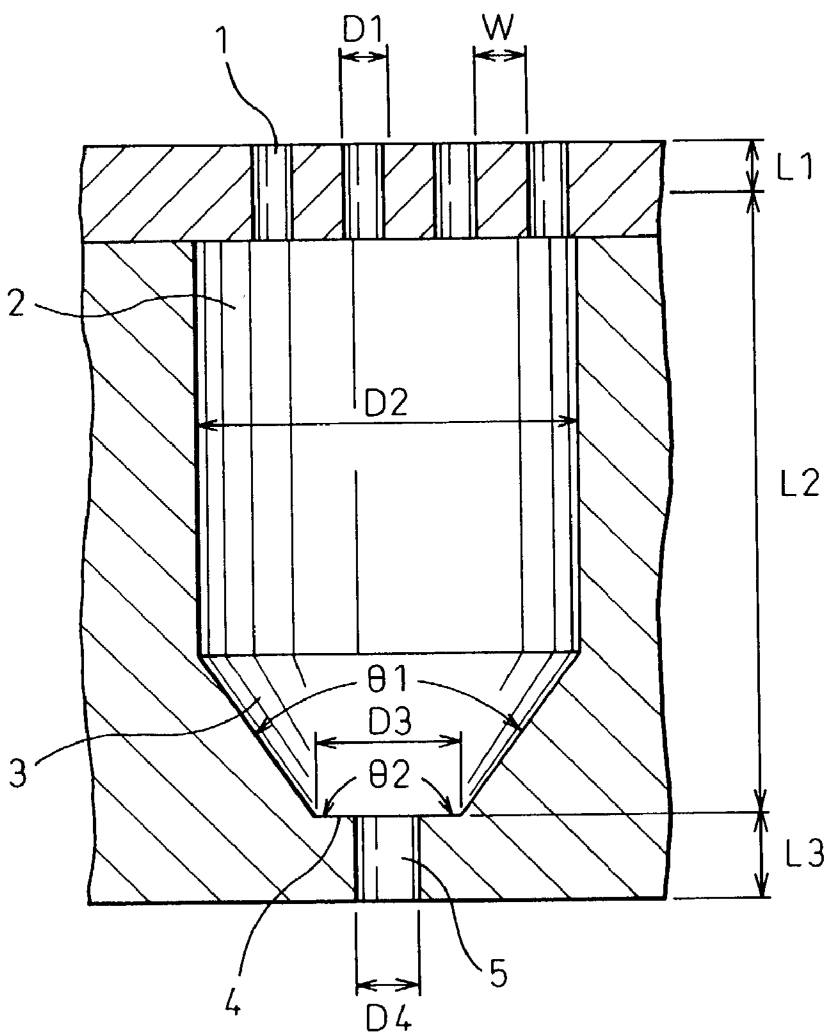


Fig.1

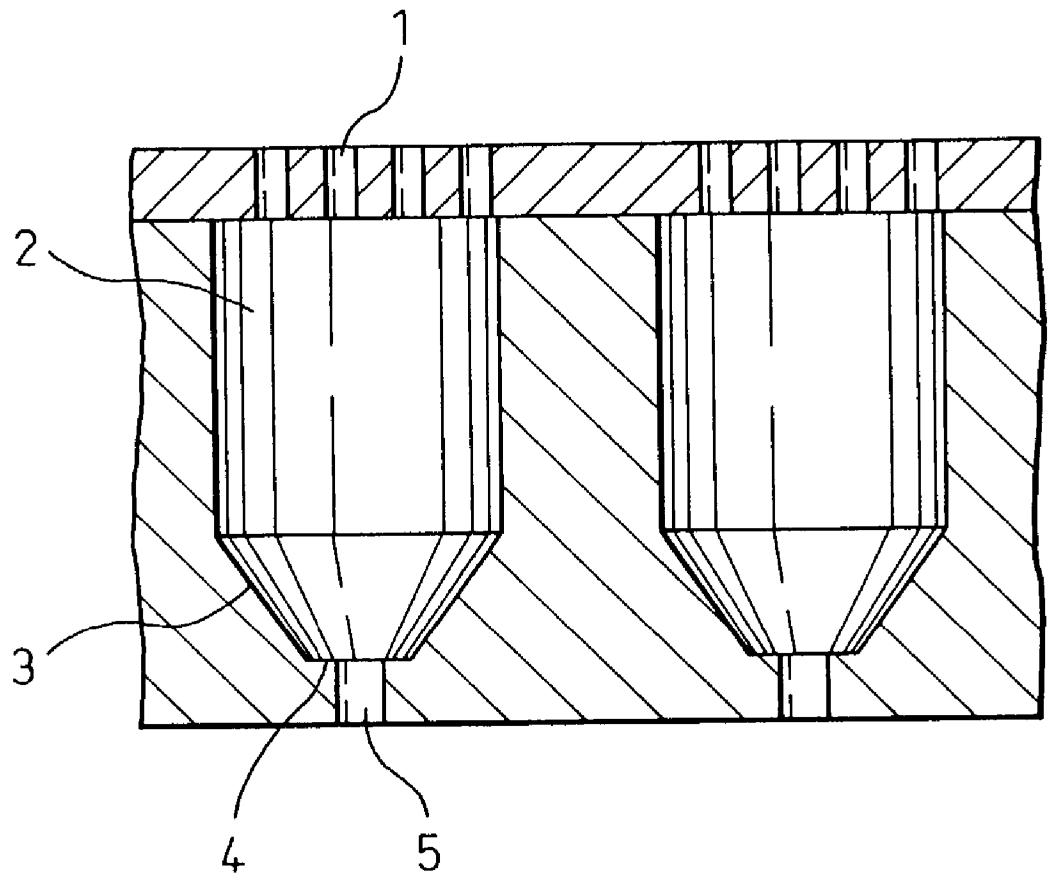


Fig. 2

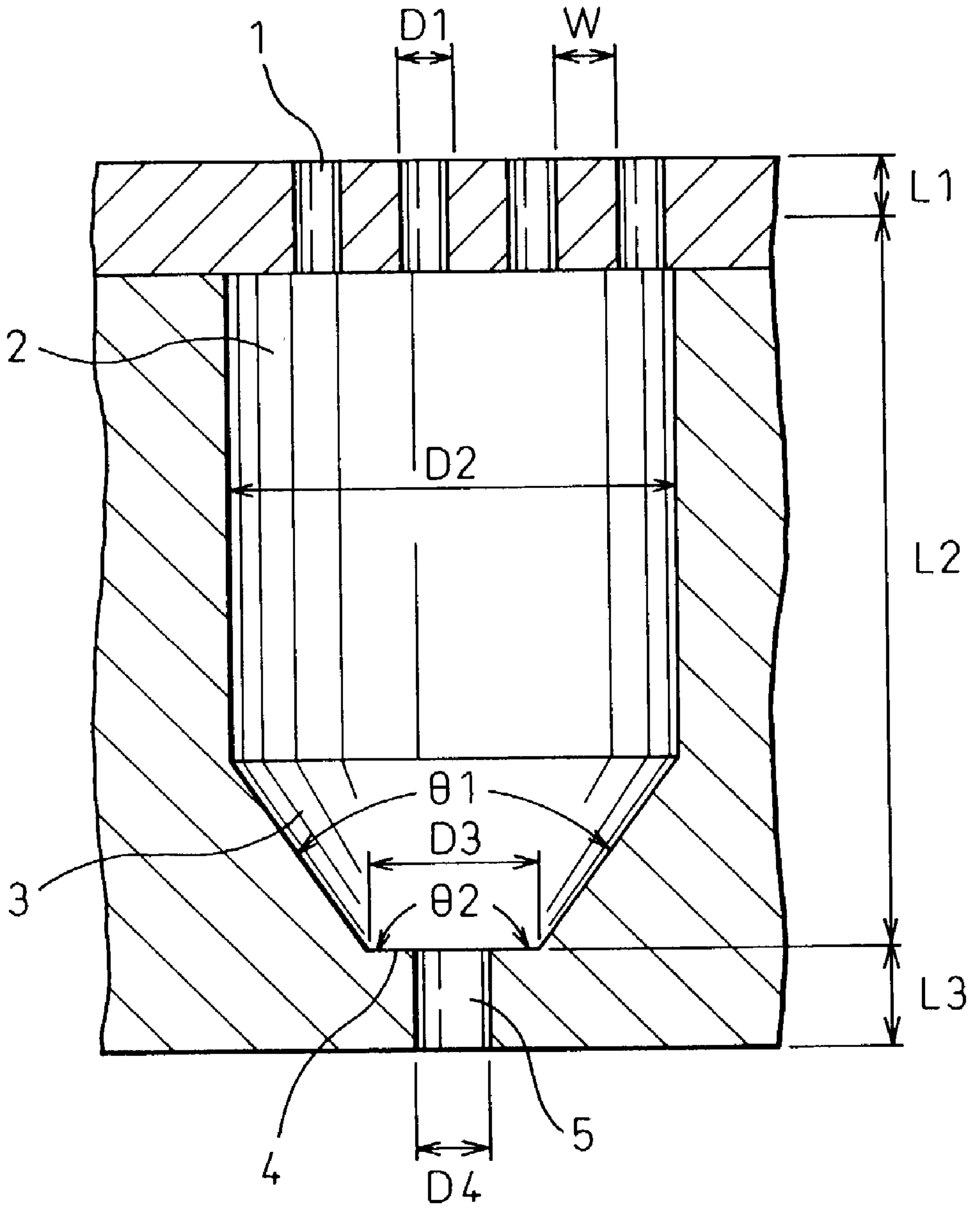


Fig. 3

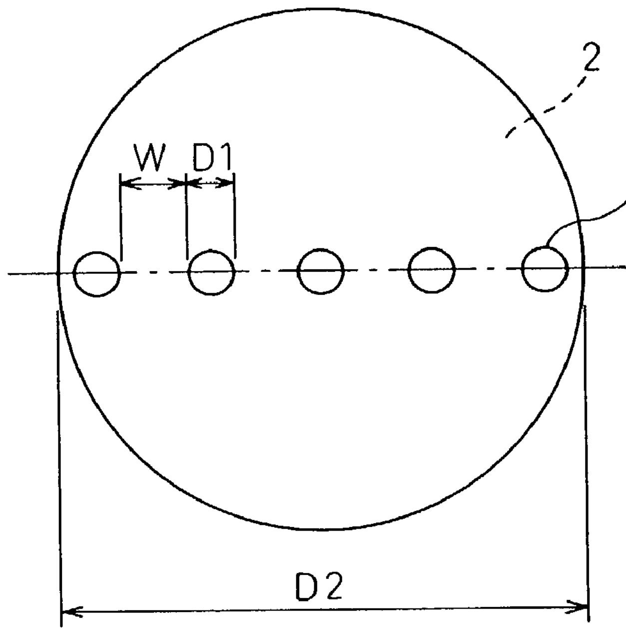
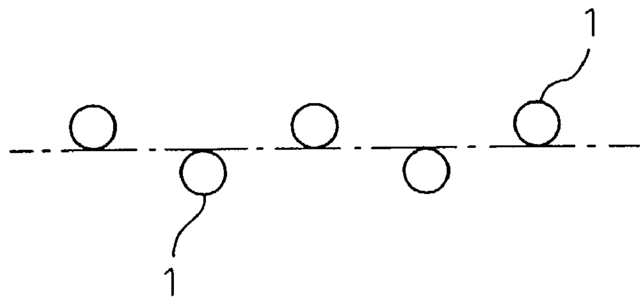
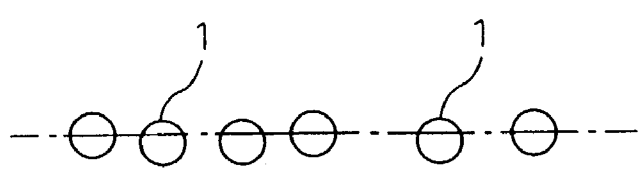


Fig. 4

(a)



(b)



METHOD FOR MANUFACTURING PITCH-BASED CARBON FIBER

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to pitch-based carbon fiber and, in particular, to a method for manufacturing pitch-based carbon fiber having a high modulus of tensile elasticity and excellent tensile and compressive strength. As the pitch-based carbon fiber provided according to the present invention has a high modulus of elasticity and high strength, the carbon fiber is suitable as reinforcing fiber for composite materials used in a variety of industrial fields, to say nothing of the fields of sports, leisure, and space and aviation.

[0003] 2. Description of the Related Art

[0004] In pitch-based carbon fiber, carbon fiber using a mesophase pitch as a starting material has an advantage that carbon fiber having an extremely high modulus of tensile elasticity can be relatively easily manufactured. The modulus of elasticity has attained a level on the order of 900 GPa substantially equal to the theoretical modulus of elasticity of graphite crystal, and carbon fiber having such a modulus of elasticity can be manufactured on an industrial scale. On the other hand, a tensile strength on the order of 3 to 4 GPa is already available. However, the practical properties such as flexural strength of a composite material are dependent on the compressive strength of fiber. The compressive strength of pitch-based carbon fiber is significantly lower than PAN-based carbon fiber, and therefore, its use for a composite material has been restricted.

[0005] With respect to such a problem, Japanese Unexamined Patent Publication No. H2-14023 discloses a method wherein carbon fiber is manufactured by spinning a pitch containing 5 to 40% of an optically anisotropic phase and having a spinning viscosity of several thousand poises, namely, a remarkably high spinning viscosity for melt spinning of pitch, thereby improving the compressive strength of the fiber. Further, Japanese Unexamined Patent Publication No. H3-816 discloses a method for improving compressive strength by implanting boron ions into pitch-based carbon fiber in a vacuum.

[0006] There are many manufacturing methods of pitch-based carbon fiber using a mesophase pitch as a raw material because these methods are variable depending on the spinning conditions. Therefore, many production methods are provided. For example, Japanese Unexamined Patent Publication Nos. S59-168127 and S60-194120 disclose a manufacturing method wherein pitch-based carbon fiber, without cracks in a cross section of the fiber, is manufactured by disposing an arcuate flow path on the upstream side of a discharge hole. Further, Japanese Unexamined Patent Publication No. H2-242918 discloses that strength is improved by changing the above-mentioned arcuate flow path to a rectangular flow path. Furthermore, Japanese Unexamined Patent Publication No. H7-42025 discloses that compressive strength is improved depending on the shape of a portion approaching a discharge hole.

[0007] However, these methods have too many problems to obtain high-performance pitch-based carbon fiber; some employ the specific manufacturing conditions, some require industrially impractical processes as compared with conventional manufacturing methods of carbon fiber, or some provide little effect on the improvement of compressive strength irrespective of improvements made on spinning methods.

SUMMARY OF THE INVENTION

[0008] The object of the present invention is to provide a method for manufacturing carbon fiber having high tensile and high compressive strength and, in particular, to provide a method for manufacturing, on an industrial basis and in a simple and easy way, pitch-based carbon fiber having high strength even in a high-elasticity domain where the modulus of elasticity exceeds 600 GPa.

[0009] The gist of the present invention is as follows:

[0010] (1) A method for manufacturing pitch-based carbon fiber by melt-spinning a mesophase pitch having optical anisotropy by using nozzles each equipped with an introduction hole entry portion, an introduction hole, an approach portion, and a discharge hole, and applying thereto infusibilization, carbonization, or graphitization, characterized in that the flow of the mesophase pitch is passed through a plurality of contraction holes disposed in a substantially straight line in the introduction hole entry portion of each nozzle, then expanded in the introduction hole, and thereafter contracted in the approach portion and then spun by being passed through the discharge hole.

[0011] (2) A method for manufacturing pitch-based carbon fiber according to the item (1), characterized in that three or more contraction holes of 0.05 to 1 mm in diameter are disposed in a substantially straight line in said introduction hole entry portion.

[0012] (3) A method for manufacturing pitch-based carbon fiber according to the item (1) or (2), characterized in that the shape of the approach portion extending from the introduction hole to the discharge hole is a conical shape having an angle of inclination of 60 to 150 degrees.

[0013] (4) A method for manufacturing pitch-based carbon fiber according to the item (1) or (2), characterized in that a flat portion is formed on the terminal end of said approach portion and a discharge hole having a circular cross-sectional shape is disposed in the flat portion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a schematic view showing a partial section of a spinning nozzle assembly used for the present invention.

[0015] FIG. 2 is an enlarged view showing a portion of the spinning nozzle assembly.

[0016] FIG. 3 is a view showing the relation between holes disposed in a straight line in an introduction hole entry portion and an introduction hole.

[0017] FIG. 4 consists of views showing examples of holes disposed in a substantially straight line in an introduction hole entry portion. **FIG. 4**(*a*) is a view showing one example, and (b) is a view showing another example.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[**0018**] The contents of the present invention will be explained in detail hereafter.

[**0019**] It is said that the strength of pitch-based carbon fiber is influenced by the fine structure of crystal grains of the fiber and also the strength changes depending on a macroscopic structure exhibited on a cross section of the fiber which is generally referred to as radial, random, onion or the like.

[**0020**] In general, a structure exhibited on a cross section of fiber is substantially determined in the stage of melt spinning. The present inventors have discovered that, in order to obtain a cross-sectional structure that increases strength, the method of spinning is required to satisfy the requirements stated below. It has also been made clear that, when the requirements stated below are satisfied, a remarkable improvement of physical properties is perceived as compared with conventional methods.

[**0021**] FIGS. **1** to **3** show partial sections of a spinning nozzle assembly used in the present invention. Three or more contraction holes **1** are disposed in a substantially straight line in an introduction hole entry portion. Melt spinning is performed as described below. A flow of a molten material is passed through the plurality of contraction holes **1** disposed in a substantially straight line, then expanded in an introduction hole **2**, thereafter contracted in an approach portion (contraction portion) **3** extending from the introduction hole **2** to a discharge hole **5** (with an angle of inclination starting at the introduction hole **2** and ending at the discharge hole **5** being 60 to 150 degrees), and then passed through the discharge hole **5** having a circular cross-sectional shape disposed in a flat portion **4** formed at the terminal end of the approach portion **3**. By performing melt spinning as described above, remarkable improvement of physical properties can be achieved.

[**0022**] By disposing the plurality of circular contraction holes **1** in a substantially straight line, such improvement of physical properties was perceived as was difficult to be obtained in the cases where a single contraction hole or rectangular contraction holes were used. Details of this mechanism have not yet been made clear.

[**0023**] It has been known that graphitized crystals constituting carbon fiber become finer when the size of domains constituting mesophase pitch is made smaller. Also, it is often said about materials in general that higher strength is obtained when the structure of crystals constituting carbon fiber is made finer.

[**0024**] From these points, it is presumed that, in the present invention, a shearing force acts on mesophase pitch in a plurality of contraction holes **1** and this shearing force makes domains finer while mutual interference of the flows of the mesophase pitch also leads to making the domains finer, thereby effectively improving the physical properties of the pitch.

[**0025**] Further, it is assumed that the pattern of interference having rectilinear shape along the contraction holes **1** gives regularity to the manner in which the cross-sectional structure of fiber is disordered, this changes the macroscopic structure of the carbon fiber, and as a result, its strength is improved; however, the details are unclear.

[**0026**] As shown in **FIGS. 2 and 3**, it is preferable that the diameter D1 of the contraction hole **1** is 0.05 to 1 mm. Still more preferably, it is 0.1 to 0.7 mm. Further, all of the contraction holes **1** are not necessarily required to have the same diameter, and different diameters can be employed properly. The number of contraction holes is **3** or more, preferably **3** to **20**, still preferably **4** to **10**. It is essential to dispose the contraction holes in a substantially straight line. Under normal conditions, it is preferable to dispose the contraction holes at equal intervals in such a manner that the diameter of the introduction hole is equally divided by the number of the contraction holes to be disposed; however, the contraction holes need not necessarily be disposed at equal intervals, but also other manners are allowable. The term "in a substantially straight line" here means that, as shown in (a) and (b) of **FIG. 4**, the group of a plurality of contraction holes **1** viewed from a direction normal to the cross section are arranged in a substantially straight line (refer to **FIG. 4**(*b*)), and also it can be said that holes arranged in zigzags in one direction, for example, are arranged in a substantially straight line (refer to **FIG. 4**(*a*)).

[**0027**] Further, it is preferable that the value obtained by dividing the diameter D1 of each contraction hole **1** in the introduction hole entry portion by the mean value of interval W between contraction holes **1** is **3** or less, still preferably **2** or less. If this value exceeds **3**, the interference between contraction holes **1** is reduced, and accordingly its effect on the improvement of strength is lessened.

[**0028**] In order to prevent any stagnating portions from developing when a contracted flow from the introduction hole **2** toward the discharge hole **5** is formed, it is a common practice to form a portion extending from the introduction hole **2** to the discharge hole **5** into a conical shape having a specific angle and to dispose the discharge hole **5** at the terminal end of the cone. This shape, however, is undesirable as it causes radial layers to develop in a surface layer portion of the fiber. When the angle θ1 of the approach portion (contraction portion) **3** shown in FIG. 2 is smaller than 40 degrees, the approach portion is inappropriately lengthened, and when the angle is larger than 150 degrees, the effect of disposing a flat portion **4** at the terminal end of the approach portion (contraction portion) **3** is hardly obtained. Further, it is preferable for the angle θ1 to be 90 to 140 degrees.

[**0029**] The diameter D2 of the introduction hole **2** is 0.5 to 10 mm, preferably 1.2 to 5 mm. Residence time in the introduction hole **2** is designed to be 1 to 400 sec., preferably 4 to 200 sec. If the diameter D2 of the introduction hole **2** is smaller than 0.5 mm or larger than 10 mm, the compressive strength of obtained carbon fiber is decreased to some extent. Likewise, if the residence time is shorter than 1 sec. or longer than 400 sec., it becomes difficult to obtain an excellent strength improving effect. It is preferable that the diameter D3 of the flat portion **4** is not larger than 0.8 times the introduction hole diameter D2 and not smaller than 1.5 times the diameter D4 of the discharge hole **5**, and the effect of the present invention can be maximized under these conditions. Further, the diameter D4 of the discharge hole **5** is 0.05 to 0.5 mm, preferably 0.08 to 0.2 mm.

[0030] Further, it is preferable for the introduction hole length L2 to be 3 to 30 mm, still preferably 4 to 15 mm. The length L3 of the discharge hole **5** is 0.05 to 3 mm, preferably 0.1 to 1 mm. The orifice length L1 of each contraction hole in the introduction hole entry portion is 0.05 to 2 mm, preferably 0.1 to 0.5 mm.

[0031] The pitch used as the starting material of the carbon fiber according to the present invention includes various kinds of pitch such as: coal-based pitch such as coal tar and coal-tar pitch; liquefied coal pitch; ethylene-tar pitch; petroleum-based pitch such as decanted oil pitch obtained from the cracked residue of a fluidized catalytic cracking process; synthetic pitch made from naphthalene and the like by using a catalyst; and the like.

[0032] The mesophase pitch used for the carbon fiber according to the present invention is made by generating a mesophase in the above-mentioned pitch by using a publicly known prior art method. It is desirable that the mesophase pitch exhibits high orientation when spun into pitch fiber, and therefore, it is desirable for the mesophase content to be 60% or higher.

[0033] Further, it is preferable that the mesophase pitch used for the present invention has a softening point of 200 to 400° C., still more preferably 250 to 350° C.

[0034] Pitch fiber is obtained by melt-spinning the above-mentioned mesophase pitch by using a spinning nozzle assembly according to the present invention. For example, pitch fiber of 5 to 20 μm in fiber diameter is obtained by drawing the above-mentioned mesophase pitch at a spinning speed of 100 to 2,000 m/min. while the mesophase pitch is extruded out of a discharge hole of 0.05 to 0.5 mm in diameter under a pressure on the order of 1 to 200 kg/cm^2 at a temperature for exhibiting a viscosity of 100 to 1,500 poises, preferably a temperature for exhibiting a viscosity of 200 to 800 poises.

[0035] After that, the pitch fiber is subjected to an infusibilizing treatment in an atmosphere of oxidizing gas, normally at a temperature of 100 to 350° C., preferably at 130 to 320° C., and normally for 10 min. to 10 hr., preferably for 1 to 6 hr. Oxygen, air, or a gas made by mixing either of them with nitrogen dioxide, chlorine or the like, is used as the oxidizing gas. The infusibilized fiber is subjected to a baking treatment at a temperature of 1,000 to 3,000° C. in an atmosphere of inert gas such as nitrogen or argon, and then a pitch-based carbon fiber of improved strength can be obtained.

[0036] The carbon fiber thus obtained has few radial components in the surface layer of the fiber and exhibits a cross-sectional structure comprising two or more kinds of structures over the entire cross section of the fiber. In cases where a single circular contraction hole is used, onion components appear relatively frequently in the cross-sectional structure of fiber. On the other hand, onion components are not so conspicuous in the structure according to the present invention. Further, if rectangular contraction holes are used, the cross section of fiber becomes relatively distorted and the uniformity of the cross-sectional structural of the fiber is lost. However, such a cross-sectional structure is not exhibited in the case of the present invention.

[0037] If a plurality of circular holes are disposed not in a straight line but in a triangle, flows from three circular holes generally interfere with each other, and a cross-sectional structure similar to that exhibited in the case where a single circular contraction hole is used is observed.

[0038] As stated above, the cross-sectional structure of the carbon fiber according to the present invention is observed to be different from that of conventional carbon fiber. The difference in the structures observable by a microscope is observed even on the level of fine graphite crystals that may determine strength and this difference seems to provide high strength.

[0039] A nozzle structure having a contraction hole in an introduction hole entry portion is apt to develop pitch stagnating portions from its structural nature. It is known that, if pitch is caused to reside for a long time at a relatively high spinning temperature, in order to prevent pitch stagnating portions from developing, a change in pitch quality locally advances to induce the generation of degradable gas or a gelatinous substance leading to thread breakage. However, it is noted that stagnating portions are prevented from developing, in the present invention, by the influence of the plurality of contraction holes. The reason for this is unclear; however, it has been found that thread breakage is apparently reduced in actual spinning according to the present invention as compared with conventional methods, and at the same time, the effects of remarkably improving the productivity and the yield of carbon fiber are obtained.

[0040] According to the present invention, it is made possible to obtain, by a relatively simple means, pitchbased carbon fiber having excellent strength, namely, a modulus of tensile elasticity of the order of 800 GPa, a compressive strength of 800 MPa or higher, and a tensile strength of 4,000 MPa. Further, the present invention also provides the effect of reducing thread breakage that is an important factor affecting the productivity of pitch-based carbon fiber.

[0041] The present invention will be explained hereafter in detail for clarifying the effects by using Examples and Comparative Examples. With respect to the measurement of compressive strength, a unidirectionally oriented composite material was prepared, the compressive strength of the composite material was measured based on ASTM-D3410, and the compressive strength of the fiber was obtained by dividing the compressive strength thus obtained by the content of fiber. Also, the modulus of torsional elasticity was then measured as a numerical value for expressing the difference in macroscopic structures exhibited on a cross section of carbon fiber. The measurement of the modulus of torsional elasticity was performed by using a method disclosed in Japanese Unexamined Patent Publication No. H7-42025. More specifically, a single fiber having a length of about 50 mm was used, and the single fiber was suspended in such a manner that one end thereof was inserted into a glass capillary tube (about 0.6 gr. in weight and 6 mm in diameter) and bonded thereto with an instantaneous adhesive, and the other end was fixed via cushion paper by a clip. Then, the glass capillary tube was turned about 30 degrees to give a twist to the fiber, thus causing the fiber to freely oscillate, and the cycle T of the oscillation was measured. The modulus Gt of torsional elasticity of fiber was calculated by the following expression:

[0042] $Gt=128\pi LI/(d^4T^2)$,

[0043] where

[0044] $I=MD^2/8$,

[0045] Gt: Modulus of torsional elasticity [Pa],

[0046] L: Length of fiber [m],

[0047] I: Torsional moment [kg/m^2],

[0048] M: Weight of capillary tube [kg],

[0049] D: Diameter of capillary tube [m],

[0050] d: Diameter of fiber [m],

[0051] T: Cycle [s].

EXAMPLE 1

[0052] Coal tar pitch, as a raw material, having a softening point of 80° C. and cleared of quinoline insolubles, was directly hydrogenerated by using a catalyst. The hydrogenated pitch was heat-treated at 490° C. under a reduced pressure, and then low-boiling point components were removed therefrom to obtain mesophase pitch. This pitch has a softening point of 298° C., insoluble toluene of 85 wt. %, insoluble pyridine of 42 wt. %, and has a mesophase content of 80%.

[0053] A nozzle assembly was used having 3,000 discharge holes **5** and being equipped with a structure (refer to **FIG. 2**) made by placing a plate on the upper portions of unit nozzles. Each of the unit nozzles has a discharge hole **5** having a diameter D4 of 0.10 mm and a length L3 of 0.15 mm, a flat portion **4** having a diameter D3 of 0.5 mm and an introduction hole **2** having a diameter D2 of 1.8 mm, an angle θ1 of 120 degrees, and a length L2 of 7 mm. As contraction holes **1**, six holes per unit nozzle, each hole having a thickness L1 of 0.5 mm and a diameter D1 of 0.2 mm, are bored through the plate at equal hole intervals W of 0.16 mm in a straight line in a diametrical direction of the introduction hole **2**.

[0054] The mesophase pitch with a viscosity of 600 poises was spun by using this nozzle assembly at a pitch fiber drawing speed of 600 m/min. to obtain pitch fiber of 9 μm in single thread diameter, and the 3,000 pieces of pitch fiber were tied up in a bundle and housed in a can.

[0055] In this event, the frequency of breakage of one or more pieces of thread was measured during the spinning of the 3,000 pieces of pitch fiber, and resultantly, the frequency of thread breakage was 300 min./time/3,000 pieces on the average.

[0056] With the pitch fiber housed in the can, an oxidizing gas made by adding gaseous nitrogen dioxide of 5 vol. % and water vapor of 5 vol. % to air was injected into the can from a lower portion of the can and the temperature in the can was increased from 150° C. to 300° C. at 1° C./min. and held at 300° C. for 30 minutes to obtain infusibilized fiber.

[0057] The temperature of the can housing the infusibilized fiber was increased to 390° C. at 10° C./min. in an atmosphere of gaseous nitrogen and held at 390° C. to primarily carbonize the infusibilized fiber. Then, the primarily carbonized fiber was further carbonized at a temperature of 1,200° C. and subsequently graphitized at a temperature of 2,700° C. to obtain carbon fiber.

[0058] This carbon fiber was 7 μm in fiber diameter, and the modulus of tensile elasticity thereof was 840 GPa, the tensile strength 4,800 MPa, and the compressive strength 950 MPa in terms of carbon fiber. A single thread was taken out of the carbon fiber and its modulus of torsional elasticity was measured and found to be 9.4 GPa. A cross section of the carbon fiber was observed by the use of a scanning electron microscope, and it was found that about 5% of the surface layer was composed of radial structures, about 20% of the middle portion was composed of onion-like structures, and the portion between the surface layer and the middle onion portion was composed of random structures.

COMPARATIVE EXAMPLE 1

[0059] A plate having a hole of 0.5 mm in diameter disposed substantially in the middle of the introduction hole was used in place of the plate used for Example 1. Spinning was conducted under the same conditions as those of Example 1. The frequency of thread breakage measured in the same way as Example 1 was 12 min./time/3,000 pieces on the average. Then, pitch fiber thus obtained was carbonized in the same way as Example 1 to obtain carbon fiber. This carbon fiber was 7 μm in fiber diameter, and the modulus of tensile elasticity thereof was 800 GPa, the tensile strength 3,900 MPa, and the compressive strength 900 MPa in terms of carbon fiber. A single thread was taken out of the carbon fiber and its modulus of torsional elasticity was measured and found to be 11.5 GPa. A cross section of the carbon fiber was observed by the use of a scanning electron microscope, and it was found that about 10% of the surface layer was composed of radial structures, and other portions were composed of onion-like structures.

COMPARATIVE EXAMPLE 2

[0060] A plate having a rectangular slit of 0.2 mm in width and 1.5 mm in length disposed substantially in the middle of the introduction hole was used in place of the plate used for Example 1. Spinning was conducted under the same conditions as those of Example 1. The frequency of thread breakage measured in the same way as Example 1 was 30 min./time/3,000 pieces on the average. Then, pitch fiber thus obtained was carbonized in the same way as Example 1 to obtain carbon fiber. This carbon fiber was 7 μm in fiber diameter, and the modulus of tensile elasticity thereof was 840 GPa, the tensile strength 4,100 MPa, and the compressive strength 900 MPa in terms of carbon fiber. A single thread was taken out of the carbon fiber and its modulus of torsional elasticity was measured and found to be 10.0 GPa. A cross section of the carbon fiber was observed by the use of a scanning electron microscope, and it was found that about 10% of the surface layer was composed of radial structures, and the other portions were composed of the mixture of onion structures and random structures.

EXAMPLE 2

[0061] Coal tar pitch, as a raw material, having a softening point of 80° C. and cleared of quinoline insolubles, was directly hydrogenenated by using a catalyst. The hydrogenated pitch was heat-treated at 490° C. under a reduced pressure, and then low-boiling point components were removed therefrom to obtain mesophase pitch. This pitch has a softening point of 298° C., insoluble toluene of 85 wt. %, insoluble pyridine of 42 wt. %, and has a mesophase content of 80%.

[0062] A nozzle assembly was used having 3,000 discharge holes **5** and being equipped with a structure (refer to **FIG. 2**) made by placing a plate on the upper portions of unit nozzles. Each of the unit nozzles has a discharge hole having a diameter D4 of 0.10 mm and a length of 0.15 mm, a flat portion having a diameter D3 of 0.5 mm and an introduction hole having a diameter D2 of 2.0 mm, an angle θ1 of 120 degrees, and a length L2 of 7 mm. As contraction holes, five holes per unit nozzle, each hole having a thickness L1 of 0.5 mm and a diameter D1 of 0.25 mm, are bored through the plate at equal hole intervals W of 0.188 mm in a straight line in a diametrical direction of the introduction hole.

[0063] The mesophase pitch with a viscosity of 400 poises was spun by using this nozzle assembly at a pitch fiber drawing speed of 700 m/min. to obtain pitch fiber of 8 μm in single thread diameter, and the 3,000 pieces of pitch fiber were tied up in a bundle and housed in a can.

[0064] In this event, the frequency of breakage of one or more pieces of thread was measured during the spinning of the 3,000 pieces of the pitch fiber, and resultantly, the frequency of thread breakage was 180 min./time/3,000 pieces on the average.

[0065] With the pitch fiber housed in the can, an oxidizing gas made by adding gaseous nitrogen dioxide of 5 vol. % and water vapor of 5 vol. % to air was injected into the can from a lower portion of the can while the temperature in the can was increased from 150° C. to 300° C. at 1° C./min. and held at 300° C. for 30 minutes to obtain infusibilized fiber. The temperature of the can housing the infusibilized fiber was increased to 390° C. at 10° C./min. in an atmosphere of gaseous nitrogen and held at 390° C. to primarily carbonize the infusibilized fiber. Then, the primarily carbonized fiber was further carbonized at a temperature of 1,200° C. and subsequently graphitized at a temperature of 2,700° C. to obtain carbon fiber.

[0066] This carbon fiber was 6 μm in fiber diameter, and the modulus of tensile elasticity thereof was 790 GPa, and the tensile strength 530 MPa. A single thread was taken out of the carbon fiber and its modulus of torsional elasticity was measured and found to be 9.0 GPa. A cross section of the carbon fiber was observed by the use of a scanning electron microscope, and it was found that about 5% of the surface layer was composed of radial structures, about 20% of the middle portion was composed of onion-like structures, and the portion between the surface layer and the middle onion portion was composed of random structures.

[0067] As is evident from Examples and Comparative Examples, according to the present invention, the strength of pitch-based carbon fiber can be improved by a technology easily applicable to industrial implementation, without requiring any special pitch or without requiring any special processing in manufacturing fiber, and carbon fiber can be obtained having a modulus of tensile elasticity on the order of 800 GPa and also excellent values of both tensile and compressive strength.

[0068] Further, according to the present invention, stability in spinning is remarkably improved and thread breakage is reduced, and therefore it is made possible to obtain extremely important industrial improvements from the aspects of both productivity and quality.

1. A method for manufacturing pitch-based carbon fiber by melt-spinning a mesophase pitch having optical anisotropy by using nozzles each equipped with an introduction hole entry portion, an introduction hole, an approach portion, and a discharge hole, and applying thereto infusibilization, carbonization, or graphitization, characterized in that the flow of the mesophase pitch is passed through a plurality of contraction holes disposed in a substantially straight line in the introduction hole entry portion of each nozzle, then expanded in the introduction hole, and thereafter contracted in the approach portion and then spun by being passed through the discharge hole.

2. A method for manufacturing pitch-based carbon fiber according to claim 1, characterized in that three or more contraction holes of 0.05 to 1 mm in diameter are disposed in a substantially straight line in said introduction hole entry portion.

3. A method for manufacturing pitch-based carbon fiber according to claim 1 or **2**, characterized in that the shape of the approach portion extending from the introduction hole to the discharge hole is a conical shape having an angle of inclination of 60 to 150 degrees.

4. A method for manufacturing pitch-based carbon fiber according to claim 1 or **2**, characterized in that a flat portion is formed on the terminal end of said approach portion and a discharge hole having a circular cross-sectional shape is disposed in the flat portion.

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