

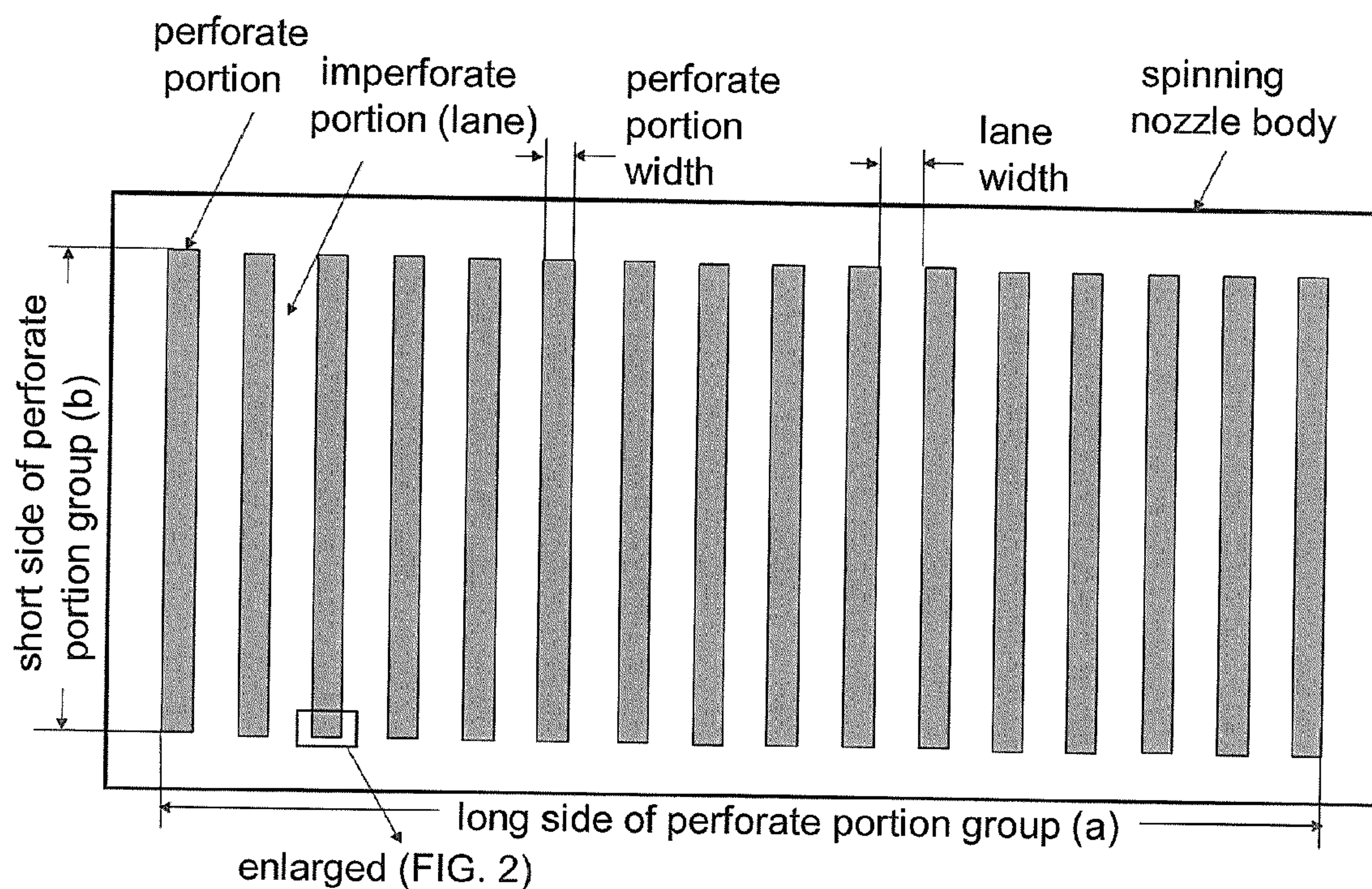
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(57) **ABSTRACT**

A carbon fiber bundle having high total fineness and extremely fine single fiber fineness is provided. The carbon fiber bundle includes continuous single fibers and satisfying the following (1) to (4): (1) a fineness of the single fiber is 0.0035-0.056 dtex; (2) a number of the single fibers in one carbon fiber bundle is 300-2500 thousand; (3) a strand strength of the carbon fiber bundle is 3000-10000 MPa; and (4) a strand elastic modulus of the carbon fiber bundle is 200-400 GPa.



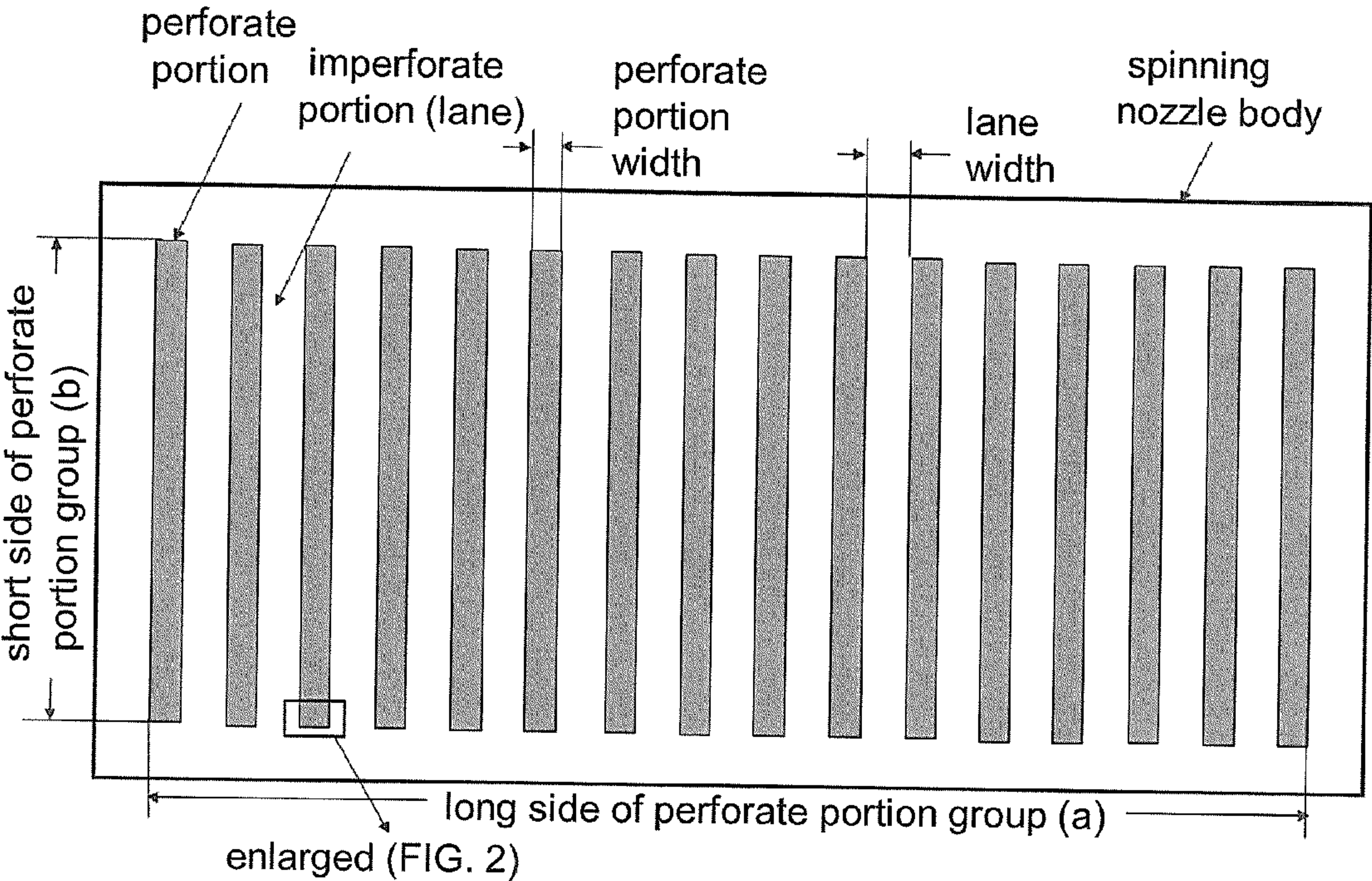


FIG. 1

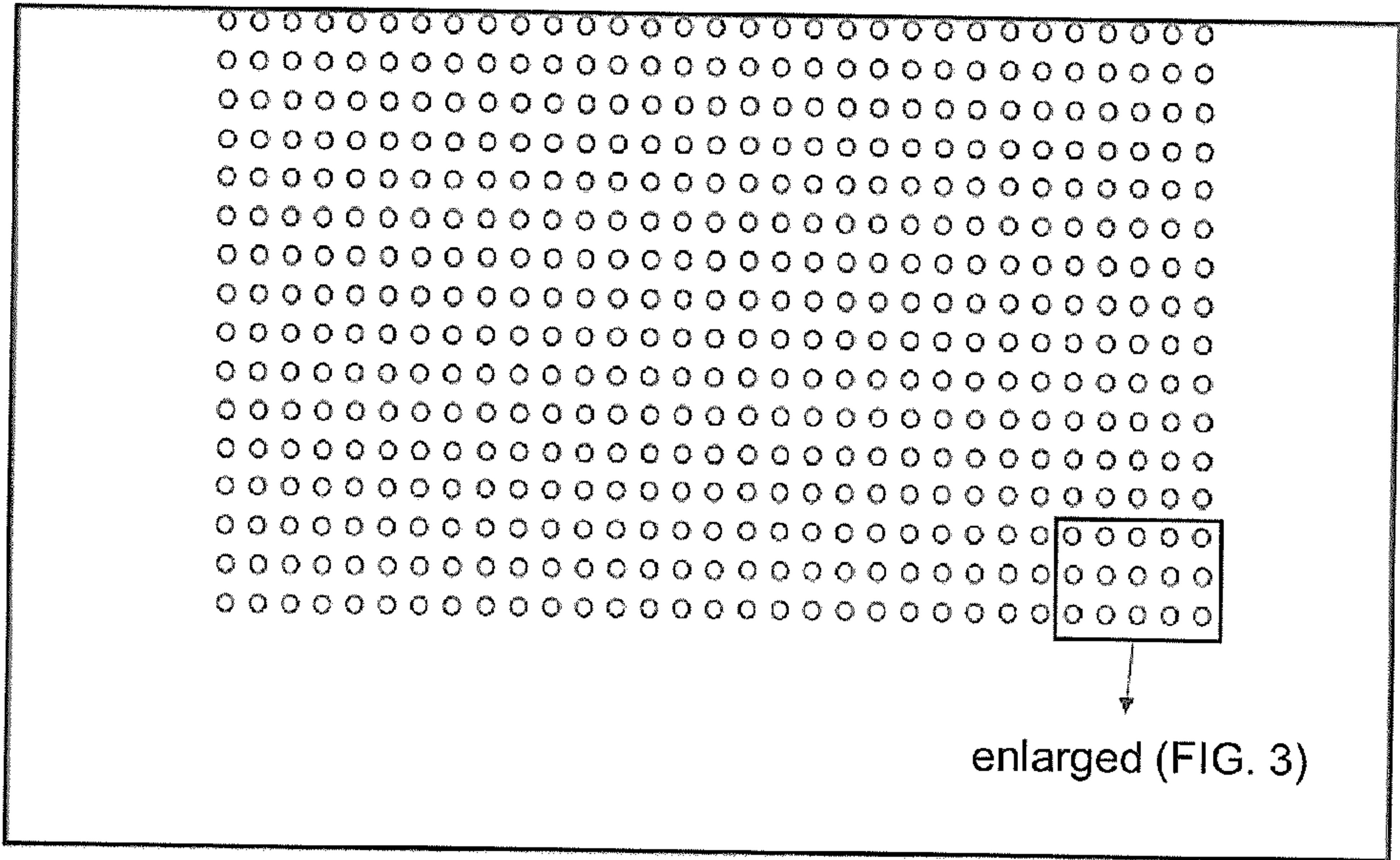


FIG. 2

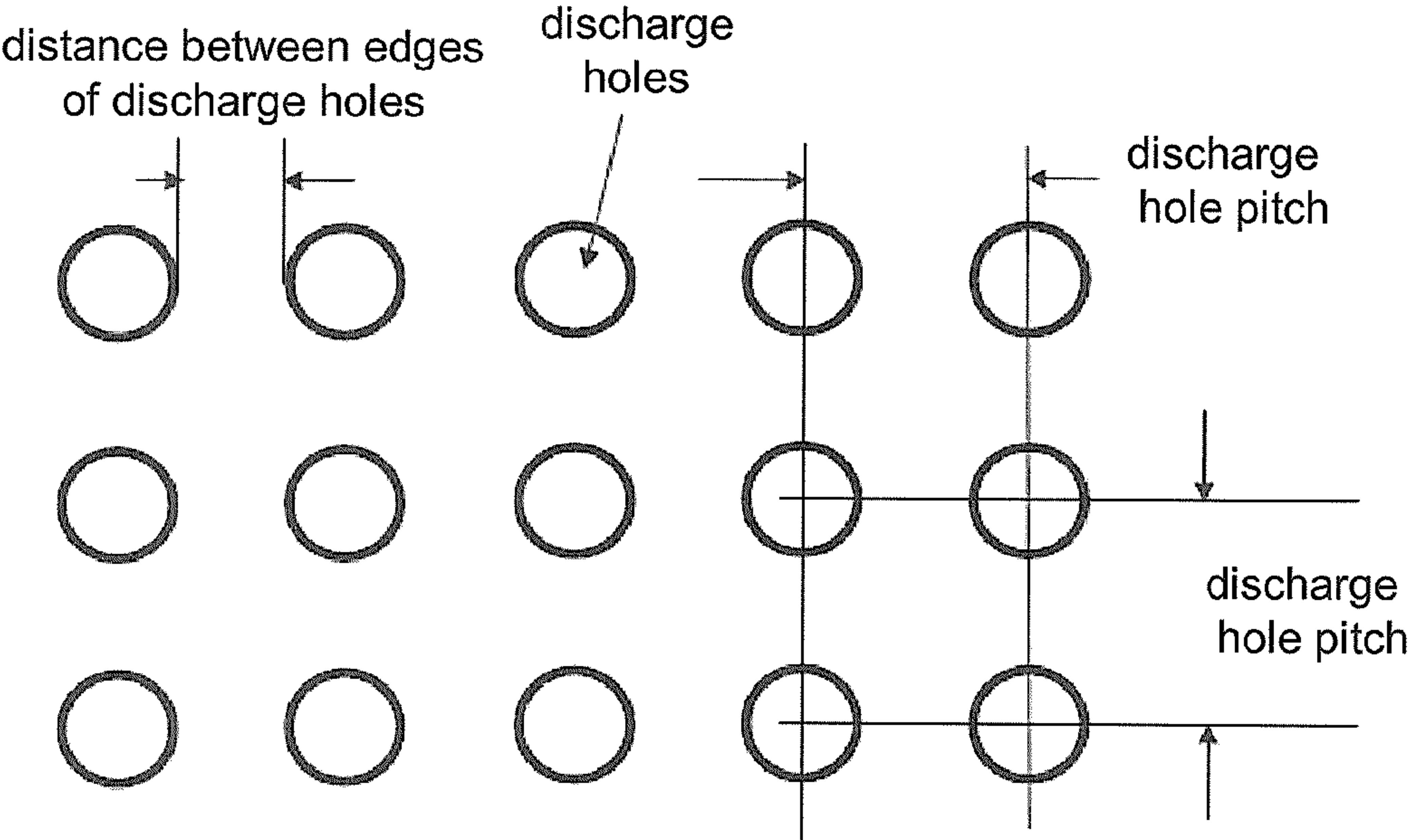


FIG. 3

CARBON FIBER BUNDLE AND METHOD FOR PRODUCING SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the priority benefit of Japan application no. 2014-172223, filed on Aug. 27, 2014. The entirety of the above-mentioned patent application is hereby incorporated by reference herein and made a part of this specification.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to a carbon fiber bundle made of uniform and continuous ultrafine carbon fibers having a diameter of less than 2 μm and a method for producing the same.

[0004] 2. Description of Related Art

[0005] Carbon fibers that are produced from polyacrylonitrile-based fibers as precursor fibers are produced by the following: after the dope of polymer solution is coagulated by a wet spinning method or a dry-wet spinning method, the polyacrylonitrile-based fibers are stretched to improve the orientation and crystallinity to obtain fibers having a diameter of 2-20 μm , and then in the subsequent stabilization process, after the polyacrylonitrile-based polymer is cyclized and oxidized, a graphite-like structure is formed by further high-temperature treatment. The carbon fibers obtained by such a method have an essential structural difference in the cross-sectional direction.

[0006] Moreover, it is considered that the structure of the precursor fibers, i.e. the polyacrylonitrile-based fibers, is an aggregation of fibrils that are hundreds of nm in diameter. Therefore, it is believed that the straightness of the fibrils may be improved and the internal void between the fibrils may be reduced by making the precursor fibers extremely fine. Accordingly, by making the precursor fibers ultrafine, the precursor fibers may have better crystal orientation and fewer voids.

[0007] From such ultrafine precursor fibers, it is possible to produce carbon fibers efficiently in a short time, and the generation of defects in the carbonization process may also be suppressed. Consequently, the carbon fibers may achieve excellent mechanical performance.

[0008] The conventional spinning method however has the limitation of about 3 μm in reducing the fiber diameter, which is insufficient to solve the aforementioned problem.

[0009] Regarding the industrial production technology of ultrafine fibers, a phase separation method has been proposed. This method is to spin and stretch fibers utilizing a composite spinning technique with use of dope that include two component polymers phase-separable from each other to form fibers composed of the two component polymers which are phase-separated from each other, and then remove one component polymer with a solvent, so as to obtain ultrafine fibers composed of the other component polymer. Since the ultrafine fibers obtained by such a method are stretched, the fiber bundle thereof has high molecular orientation and high crystallinity and crystal orientation.

[0010] For this method, however, it is necessary to remove a large amount of the component polymer, which increases the costs. Further, the total fineness of the fiber bundle obtained from a single nozzle would be low. Thus, a large

number of nozzles would be needed in order to obtain a carbon fiber bundle of high total fineness and enormous equipment investment is required to industrialize this technique. For these reasons, this technique has not been used for industrial use.

[0011] There is an electrospinning method, which is also a technique of producing ultrafine fibers. This method produces fine fibers by accumulating electronic charges in the dielectric in the injection nozzle and applying a high voltage between the injection nozzle and the counter electrode when discharging the polymer solution from the injection nozzle, so as to disperse and make the polymer solution fine by the electrostatic repulsive force. In this case, because the solvent of the polymer solution is discharged outside the fibers, the accumulated ultrafine fibers contain little solvent. Thus, a substantially dry ultrafine fiber aggregate is formed immediately after the spinning. It is a simple and easy production method.

[0012] However, like the phase separation method described above, the electrospinning method requires a very large number of nozzles in order to obtain a carbon fiber bundle having high total fineness. Enormous equipment investment is required for producing the carbon fiber bundle having high total fineness, and therefore such equipment has not been used for industrial use.

[0013] Regarding the production method of ultrafine fibers by a wet spinning method, the following techniques have been disclosed.

[0014] Patent Literature 1 discloses a spinneret and a production method of acrylic fibers and discloses that acrylic-based fibers having single fiber fineness of 0.0333-55.5 dtex are obtained by setting the hole density to 3-35/ mm^2 .

[0015] Patent Literature 2 discloses an ultrafine fiber aggregate, a production method thereof, and a production apparatus thereof, and discloses to obtain an ultrafine organic fiber bundle having 0.011-0.56 dtex, large irregularities and poor uniformity in the fiber cross section by wet spinning through using a spinneret made of a metal fiber-made sheet sintered plate that has a filtration accuracy of 15 μm or more.

[0016] Patent Literature 3 discloses a carbon fiber bundle consisting of 170,000 single fibers having a diameter 2.1 μm .

PRIOR ART LITERATURE

Patent Literature

[0017] [Patent Literature 1] Japanese Patent Publication No. 2000-328347

[0018] [Patent Literature 2] Japanese Patent Publication No. S51-119826

[0019] [Patent Literature 3] Japanese Patent Publication No. 2009-256816

SUMMARY OF THE INVENTION

Problems to be Solved

[0020] In order to manufacture without significant reduction in the productivity, an effective way to produce ultrafine fibers by the conventional wet spinning method is to increase the number of discharge holes on each spinneret. Increasing the area of the discharge surface having the discharge holes is considered a method for increasing the number of holes of the spinning nozzles. However, if the area of the discharge surface of the spinning nozzles is made too large, it is difficult to keep the solvent concentration of the coagulation liquid at or

below the specified concentration in the region of the discharge hole groups arranged in the central portion of the discharge surface of the spinning nozzles, and defects may occur in the fiber filaments formed from these discharge holes. Problems such as deformation (swelling) of the discharge surface due to the discharge pressure of the dope may also occur. In addition, the spinning nozzles cannot be accommodated into the existing coagulation bath, and it would be necessary to fabricate a new coagulation bath. Thus, it is required to manufacture the coagulation bath equipment and secure the location for disposing the equipment.

[0021] Under these circumstances, in order to suppress the equipment investment, it is advisable to arrange the discharge holes at a high density rather than to increase the spinning nozzle discharge area.

[0022] To arrange the discharge holes of the spinning nozzles at a high density, it is necessary to narrow the discharge hole pitch, but it may easily result in adhesion between adjacent fibers because the discharge hole pitch is too narrow. In particular, in the region of the discharge hole groups arranged in the central portion of the discharge surface of the spinning nozzles, it would be difficult to keep the solvent concentration of the coagulation liquid at or below the specified concentration, and defective fiber may be formed from the discharge holes. In other words, a fiber aggregate of several or hundreds of filaments adhered to each other may be generated.

[0023] With any of the methods disclosed in Patent Literatures 1-3, it is not possible to obtain a carbon fiber bundle including 300,000 ultrafine carbon fiber filaments or more.

[0024] In view of the above, the invention provides a carbon fiber bundle having high total fineness and extremely fine single fiber fineness.

Means for Solving the Problems

[0025] According to the first aspect of the invention, a continuous carbon fiber bundle satisfies the following (1) to (4):

[0026] (1) A fineness of a single fiber is 0.0035-0.056 dtex.

[0027] (2) The number of the single fibers in one carbon fiber bundle is 300-2500 thousand.

[0028] (3) A strand strength of the carbon fiber bundle is 3000-10000 MPa.

[0029] (4) A strand elastic modulus of the carbon fiber bundle is 200-400 GPa.

[0030] According to the carbon fiber bundle of the invention, the single fiber is preferably an independent single fiber.

[0031] According to the carbon fiber bundle of the invention, the fineness of the single fiber is preferably greater than 0.0054 dtex.

[0032] According to the second aspect of the invention, a polyacrylonitrile-based carbon fiber bundle consists of continuous single fibers, a crystal orientation π (%) and a graphite crystal size L_c (nm) of which obtained by a wide-angle X-ray diffraction method satisfy the following formula (1):

$$77 \leq \pi - 3.8 \times L_c \leq 80 \quad \text{formula (1)}$$

[0033] According to the third aspect of the invention, a polyacrylonitrile-based carbon fiber bundle consists of continuous single fibers, a graphite crystal size L_c (nm) of which obtained by a wide-angle X-ray diffraction method and a strand elastic modulus E (GPa) satisfy the following formula (2):

$$3.28 \leq -1.05 \times 10^{15} \times E^2 + 0.0194 \times E - L_c \leq 3.94 \quad \text{formula (2)}$$

[0034] Further, the invention provides a production method of a carbon fiber bundle, the production method including: preparing dope by dissolving an acrylonitrile-based polymer in a solvent, wherein the acrylonitrile-based polymer is obtained by copolymerizing 96 mass % or more of acrylonitrile and a monomer, which is selected from a (meth)acrylic acid derivative, an itaconic acid derivative, and a (meth)acrylamide derivative, as a copolymer component; discharging the dope from a spinneret into a coagulation liquid to coagulate the discharged dope to obtain a coagulated thread, wherein the spinneret includes a perforate portion including a plurality of discharge holes that are arranged and an imperforate portion without discharge hole, and a discharge hole density of the perforate portion including the discharge holes is 600-1200/mm² and the number of the discharge holes is 300-2500 thousand; after stretching the coagulated thread 1.0-1.5 times, performing stretch and wash to stretch the coagulated thread to a range of 1.5-6 times in a washing and stretching bath including 2-10 steps having a temperature in a range of 50-100° C. and applying an oil agent including a silicone-based compound as a main component; drying the coagulated thread by passing the coagulated thread through a plurality of heating rollers and then heating the coagulated thread at a temperature of 130-200° C. to stretch the coagulated thread 1.3-7.0 times to obtain a polyacrylonitrile-based carbon fiber precursor fiber bundle having a total stretching ratio of 2-16 times; heating in an oxidizing atmosphere to perform a stabilization process on the polyacrylonitrile-based carbon fiber precursor fiber bundle; and heating in an inert atmosphere to carbonize the polyacrylonitrile-based carbon fiber precursor fiber bundle.

Effects of the Invention

[0035] According to the invention, a carbon fiber bundle made of ultrafine carbon fibers and having high total fineness may be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036] FIG. 1 is a schematic diagram showing an example of arrangement of the discharge holes on the entire spinneret.

[0037] FIG. 2 is a schematic diagram showing an example of arrangement of the discharge holes by enlarging a portion of the perforate portion.

[0038] FIG. 3 is a schematic diagram showing an example of arrangement of the discharge holes by further enlarging a portion of FIG. 2.

DESCRIPTION OF THE EMBODIMENTS

[0039] In a carbon fiber bundle of the invention, the number of single fibers is 300,000 to 2,500,000, and the single fiber fineness is 0.0035 dtex to 0.056 dtex. Performance of the carbon fibers may become unstable if the single fiber fineness is less than 0.0035 dtex. It results from that the acrylonitrile-based precursor fiber used as the raw material has a fibril structure of about 200 nm. In other words, the size of the precursor fiber itself is close to the size of the basic component structure and a stable homogeneous fine structure is not formed. Since the precursor fibers of the carbon fiber bundle of the invention are produced by the same method as precursor fibers of normal fineness in the coagulation process, the precursor fibers have a fine structure that is substantially the same as that of the fibers of normal fineness. If the single fiber fineness exceeds 0.056 dtex, uncoagulated threads near the

spinning nozzles may easily adhere (agglutinate) to each other. Preferably, the single fiber fineness is in a range of 0.006 dtex to 0.031 dtex. It is preferable that the number of single fibers is 500,000 to 1,500,000.

[0040] The carbon fiber bundle of the invention has a strand strength of 3000-10000 MPa. In addition, the strand elastic modulus thereof is 200 GPa to 400 GPa.

[0041] Preferably, the single fiber of the carbon fiber has a diameter of 0.50 μm to 1.99 μm . More preferably, the diameter of the single fiber of the carbon fiber is 0.65 μm to 1.50 μm .

[0042] Production of the carbon fiber bundle of the invention may be carried out as described hereinafter.

[Production of Carbon Fiber Precursor Fiber Bundle]

[0043] A dope containing a polyacrylonitrile copolymer is discharged from a spinning nozzle into a coagulation liquid to form a coagulated thread, and then the coagulated thread is washed and further stretched. Following that, after an oil agent process, the coagulated thread is dried and then undergoes a stretching process to form a carbon fiber precursor fiber bundle.

[Polyacrylonitrile-Based Copolymer]

[0044] The polyacrylonitrile-based copolymer is obtained by copolymerizing 96 mass % or more of acrylonitrile with a (meth)acrylic acid derivative, e.g. (meth)acrylic acid, methyl (meth)acrylate, or (meth)acrylic acid hydroxyalkyl; an itaconic acid derivative, e.g. itaconic acid or itaconic acid ester; and/or a (meth)acrylamide derivative, e.g. (meth)acrylamide, N-methylol (meth)acrylamide, or N,N-dimethyl (meth)acrylamide.

[0045] The number of the (meth) acrylic acid derivative, itaconic acid derivative, and (meth) acrylamide derivative that are copolymerized may be one or plural.

[Dope]

[0046] The polyacrylonitrile-based polymer described above is dissolved in a solvent to obtain the dope. The solvent may be an organic solvent or an inorganic solvent, which is not particularly limited. It is preferred that the solvent is an organic solvent selected from dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. These organic solvents do not contain a metal component and are capable of reducing the content of the metal component in the obtained carbon fiber bundle. In this case, it is adequate to set the solid content concentration of the dope to a range of 14-24 mass %. Then, this dope is discharged from the spinning nozzle into a coagulation bath filled with a mixed solution (the coagulation liquid) of the solvent and water. This is the so-called wet spinning method. Here, it is preferred to set the solvent concentration of the coagulation liquid to a range of 25-85 mass %.

[0047] Considering stability of the spinning, the viscosity of the dope at 50° C. is 30-200 poise preferably.

[Spinning Nozzle]

[0048] The spinning nozzle has a perforate portion, in which the number of the discharge holes is 600-1,200/ mm^2 .

[0049] FIG. 1 is a schematic diagram showing an example of arrangement of the discharge holes.

[0050] The perforate portion is a portion where a plurality of discharge holes 3 is arranged together in a specific pattern.

In a perforate portion 2 of the invention, the number of the discharge holes that exist in an area of 1 mm^2 is 600 to 1,200. A line is drawn along edges of the discharge holes 3 disposed on the outer periphery of the perforate portion 2 to serve as a perforate portion outer peripheral line, and the area surrounded by the perforate portion outer peripheral line is a perforate portion area.

[0051] Preferably, the spinning nozzle 1 includes two or more perforate portions 2 and an imperforate portion 4 therebetween. The imperforate portion 4 allows the coagulation liquid of the specific concentration to reach the dope discharged from the central portion of the perforate portion 2. The perforate portion may be in any shape as long as the perforate portion can be arranged efficiently and the coagulation liquid can flow properly. Though not particularly limited, it is more preferable to form the perforate portion into a rectangular shape. Further, it is more preferable to arrange the perforate portions such that the long sides of the rectangles are parallel to each other.

[0052] The spinning nozzle of FIG. 1 has 16 perforate portions. Nevertheless, the number of the perforate portions disposed thereon is not limited to 16. In addition, although the spinning nozzle has a rectangular shape in FIG. 1, the spinning nozzle may also be circular. The purpose of the invention may be achieved sufficiently if the shape or arrangement of the perforate portions is properly designed. In the case where the space of the coagulation bath remains the same, the total hole number per nozzle of the rectangular nozzle is larger than that of a circular nozzle and therefore the rectangular nozzle is advantageous in production efficiency.

[0053] If the number of the discharge holes per 1 mm^2 in the perforate portion is 600 or more, the size of the spinning nozzle 1 is not too large, and the ultrafine fibers may be produced at a coagulation bath of a proper scale. If the number of the discharge holes per 1 mm^2 is 1200 or less, adhesion between the single fibers may be suppressed. The lower limit of the number of the discharge holes per 1 mm^2 is preferably set to 700 or more, and more preferably 800 or more. The upper limit of the number of the discharge holes per 1 mm^2 is preferably set to 1100 or less, and more preferably 1000 or less.

[0054] It is preferable that the area of one discharge hole 3 of the spinning nozzle is 100 μm^2 or more and 350 μm^2 or less. If the area of one discharge hole 3 is 100 μm^2 or more, the discharge hole is not easily clogged with foreign matter and the production may be carried out within proper range of a dope filtration process. Further, if the area of one discharge hole 3 is 350 μm^2 or less, the produced fibers may have the desired fineness. The lower limit of the area of one discharge hole 3 is preferably set to 150 μm^2 or more, and more preferably 200 μm^2 or more. In addition, the upper limit of the area is preferably set to 300 μm^2 or less, and more preferably 250 μm^2 or less.

[0055] Preferably, the number of the discharge holes of one spinning nozzle is 300,000 to 2,500,000. If the number of the discharge holes is 300,000 or more, the desired productivity may be ensured. Moreover, if the number of the discharge holes is 2,500,000 or less, adhesion between the fibers may be suppressed to stabilize the quality of the produced fibers.

[0056] Preferably, the lower limit of the number of the discharge holes is 500,000 or more. Preferably, the upper limit of the number of the discharge holes is 2,000,000 or less.

[0057] In the spinning nozzle 1, as shown in FIG. 3, a distance L1 between the edges of adjacent discharge holes is

preferably 10 μm or more and 20 μm or less. The discharge hole **3** may have a square shape, a circular shape, or a combination of the foregoing, for example. If the distance L1 is 10 μm or more, the coagulation liquid may easily flow between coagulated threads discharged from the discharge holes **3**. If the distance L1 is 20 μm or less, the hole arrangement density of the perforate portion may remain high and the fibers of the invention may be produced efficiently without increasing the size of the nozzle. The lower limit of the distance between the edges of two discharge holes **3** is preferably set to 12 μm or more, and the upper limit is preferably set to 17 μm or less.

[0058] A detailed design of the spinning nozzle is important. Particularly, in order that the coagulation liquid can fully penetrate into the central portion of the perforate portion of the spinning nozzle, it is important to design the lengths of the short side and long side of the perforate portion of the spinning nozzle and the interval (referred to as a lane width hereinafter) between adjacent perforate portions as shown in FIG. 1. The shape and size of the proper perforate portion are influenced by the hole arrangement density, the dope (viscosity), and wet coagulation conditions (coagulation concentration and temperature). The width (the length in the transverse direction of FIG. 1) of the perforate portion is preferably set to 4 mm or less. Moreover, it is preferable to set the lane width to 1.0 mm or more. If the lane width is 1.0 mm or more, the coagulation liquid may flow easily between the perforate portions. As a result, the coagulation liquid flows to the center of the perforate portion easily. The lane width is preferably set to 2.0 mm or more, and more preferably 3.0 mm or more. On the other hand, the nozzle size increases as the lane width increases. For this reason, it is preferable to set the lane width to 10 mm or less, more preferably 7 mm or less, or even more preferably 5 mm or less.

[0059] Preferably, the length (the length in the vertical direction of FIG. 1) of the perforate portion is 50 mm or less.

[0060] An electroforming method is preferred for forming the discharge holes of the spinning nozzle. By using the electroforming method, the hole diameter may be reduced to about several μm , and the distance between the edges of adjacent discharge holes may be set to about 10 μm .

[JS Value]

[0061] In the production of the carbon fiber precursor fiber, the JS numerical condition represented by the ratio of the speed of extracting fibers from the coagulation bath to the linear speed of the dope discharged from the holes of the spinning nozzle significantly affects the stability of the production process and the properties of the carbon fiber precursor fiber obtained.

$$\text{JS value} = (\text{fiber extraction speed}) / (\text{linear speed of the discharged dope})$$

[0062] It is known that when the JS value is large, the coagulated threads tend to have a sparse structure due to the large stretching in the coagulation process. In addition, it is found that if the carbon fiber precursor fiber has a dense structure, the carbon fiber using the carbon fiber precursor fiber as the raw material exhibits excellent mechanical performance. Accordingly, in the production of precursor fibers for producing carbon fibers with general fineness, the JS value is set relatively low and does not exceed 2.5.

[0063] In contrast thereto, in the production of a carbon fiber precursor fiber bundle for ultrafine carbon fibers, when the aforementioned spinning nozzle is used, even if the JS

value is 2.5 or more, the subsequent stretching condition may be controlled properly to foam a carbon fiber precursor fiber bundle having a dense structure. The upper limit of the JS value is preferably set to 5.0 or less, and more preferably 4.0 or less.

[Washing and Stretching]

[0064] Preferably, the coagulated thread extracted from the coagulation bath is stretched 1.0 to 1.5 times in the air. Here, the stretching range of 1.0 to 1.5 times is preferable for forming a dense structure. The reason is that if the coagulated thread is stretched over 1.5 times, the coagulated thread is excessively stretched and void formation due to the stretching becomes excessive, which reduces the density of the resulting precursor fiber bundle. A more preferable range is 1.0 to 1.3 times.

[0065] After stretching in the air, it is preferable to stretch the fiber in a stretching liquid before washing, wherein the stretching liquid has a low solvent concentration and a high temperature in comparison with the coagulation liquid. The temperature of the stretching liquid is preferably in a range of 40° C. to 80° C. If the temperature is below 40° C., stretchability cannot be ensured and inhomogeneous stretching may occur, and a uniform fibril structure may not be formed. On the other hand, if the temperature exceeds 80° C., the plasticization operation subject to the heat may be too strong or the removal of the solvent from the yarn surface may proceed rapidly, which causes the stretching to be non-uniform, and a homogeneous fiber may not be produced. More preferably, the temperature is 50° C. to 75° C. In addition, it is preferred to set the solvent concentration of the stretching liquid to a range of 10 mass % to 60 mass %. If the solvent concentration is below 10 mass %, stable stretchability cannot be ensured; and if the solvent concentration exceeds 60 mass %, the plasticization effect may become excessively strong and impair the stable stretchability. A more preferred concentration is 35 mass % to 55 mass %. Preferably, the stretching ratio in the stretching liquid is 1.5 to 6.0 times. If the stretching ratio is less than 1.5 times, the stretching may be insufficient and the desired fibril structure may not be formed. On the other hand, if the fiber is stretched over 6 times, the fibril structure itself may be broken and result in carbon fiber precursor fibers in a very sparse structure form. More preferably, the stretching ratio is 2.0 to 5.5 times.

[0066] Next, washing is performed to remove the solvent. Generally, the washing is performed using water as the washing liquid. The temperature of the washing liquid is in a range of 50° C. to 100° C.

[0067] The washing process may include 2 to 10 baths. The temperature of each bath is set depending on the purpose.

[0068] In the case where stretching is performed after washing, the fiber is preferably stretched 0.97 times to 1.6 times in hot water. If the stretching is over 1.6 times, the stretching is excessive. The fibril structure may be damaged, which causes defects in the carbonization process. Preferably, the stretching range is 0.97 to 1.3 times, and more preferably the stretching range is 0.97 to 1.15 times. In this stage, distortion of the stretching in the previous process may be removed by performing some relaxation.

[0069] Besides, it is possible to perform the washing and stretching simultaneously. In that case, stretching of 1.5 to 6.0 times is preferable. More preferably, some relaxation may be performed in hot water in the final stage of the washing.

[Application of Oil Agent]

[0070] Then, 0.8 mass % to 2.0 mass % of an oil agent including a silicone-based compound as main component is applied. Regarding the composition of the oil agent with the silicone-based compound as the main component and the method of applying the oil agent, the known method that has been used for producing carbon fibers with general fineness may be adopted.

[Dry Densification and Post-Stretching]

[0071] Dry densification is performed after the oil agent is applied. The conventional method that has been used for producing a carbon fiber precursor fiber with general fineness may be used for performing the dry densification. Preferably, it is a drying method using a plurality of heating rollers.

[0072] The dried and densified fiber bundle, if necessary, may be stretched 1.3 to 7.0 times in a hot heating medium, such as pressurized steam or dry air at 130° C. to 200° C., or between the heating rollers or on a heating plate, so as to further improve the orientation and achieve densification. The method using pressurized steam as the heating medium is a more preferable stretching method since the polyacrylonitrile-based polymer may be plasticized by the steam to give a stable stretching.

[Total Stretching Ratio]

[0073] As described above, multi-stage stretching is performed and the total stretching ratio thereof is 2 to 16 times. If the total stretching ratio is less than 2 times, the stretching may be insufficient and the fibril structure oriented in the fiber axial direction may not be sufficiently developed. On the other hand, if the total stretching ratio exceeds 16 times, the fibril structure is likely to be damaged. It is preferred to adjust each stretching ratio to make the total stretching ratio fall in this range.

[Method of Producing Carbon Fiber]

[0074] A carbon fiber precursor fiber bundle is obtained by the aforementioned production method, and further a carbon fiber bundle of the invention may be obtained by the method described below.

[Stabilization]

[0075] The carbon fiber precursor fiber bundle is heated at a temperature of 220° C. to 260° C. in an oxidizing atmosphere to form a bundle of stabilized yarn (flame-resistant fiber bundle) with a density of 1.340 g/cm³ or more and 1.430 g/cm³ or less. If the density of the stabilized yarn that constitutes the stabilized fiber bundle is less than 1.340 g/cm³, the stabilization processing is insufficient and an excessive decomposition reaction may occur due to the subsequent high-temperature heat treatment, resulting in formation of defects. And, high-strength carbon fibers are not formed. If the density of the stabilized yarn exceeds 1.430 g/cm³, since the oxygen content in the fibers increases, a reaction of loss of oxygen occurs due to the subsequent high-temperature heat treatment. Defects are formed due to this decomposition reaction and consequently high-strength carbon fibers are not formed. It is more preferable to set the density range of the stabilized yarn to 1.340 g/cm³ to 1.400 g/cm³.

[0076] In the stabilization process, the cyclization reaction and the oxidation reaction due to oxygen take place at the

same time, and it is important to balance the two reactions. Regarding diffusion of oxygen into the ultrafine single fibers, because the required diffusion distance is short, it is possible to perform the process in a short time. However, if the fiber bundle includes a very large number of single fibers, the diffusion of oxygen into the fiber bundle may be limited. Thus, it is preferable to keep the single fibers sufficiently dispersed. In order to balance the two reactions, the time of stabilization processing for the ultrafine fibers is preferably 3 to 100 minutes. It is preferred to be 3 minutes or more for oxygen to diffuse sufficiently into the fiber bundle. On the other hand, if the stabilization processing is performed over 100 minutes, more oxygen exists in the portion near the surface of the single fibers, a reaction of loss of excessive oxygen occurs due to the subsequent high-temperature heat treatment, and defects are formed. Thus, high-strength carbon fibers are not formed. More preferably, the stabilization processing time is 17 to 80 minutes.

[0077] In the stabilization process, a stretching operation of -10.0% to 5% is performed. It is to maintain and improve the orientation of the fibril structure forming the fibers. In the case where the stretching is less than -10.0% (shrinkage of more than 10%), the orientation of the fibril structure cannot be maintained, and in the process of structural change during the structure formation of the carbon fibers, the orientation of the crystal in the fiber axial direction collapses greatly and the performance of the carbon fibers decreases significantly. On the other hand, in the case where the stretching exceeds 5%, the fibril structure itself is broken, and the subsequent structure formation of the carbon fibers is impaired. Moreover, the breaking points become defects and thus high-strength carbon fibers may not be obtained. More preferably, the stretching rate is -8.0% to 3%.

[Carbonization]

[0078] The stabilized fiber bundle obtained by the stabilization processing is heated by a first carbonization furnace that has a temperature gradient of 300° C. to 800° C. in an inert atmosphere, such as nitrogen, while being stretched 2% to 7%. The starting temperature is preferably 300° C. or more, and the temperature is raised monotonously. The fiber bundle becomes very brittle if the maximum temperature exceeds 800° C. A more preferable temperature range is 300° C. to 750° C. It is preferable to raise the temperature linearly with the temperature gradient being substantially constant.

[0079] In the case where the stretching is less than 2%, the orientation of the fibril structure cannot be maintained, and the crystal orientation along the fiber axis during the structure formation of the carbon fibers may not increase sufficiently. On the other hand, in the case where the stretching exceeds 7%, the fibril structure itself is broken, and the subsequent structure formation of the carbon fibers is impaired. Moreover, the breaking points become defects and thus high-strength carbon fibers may not be obtained. The stretching rate is more preferably 2% to 5%. The preferable processing time is 0.4 to 2.0 minutes. In the case where the processing is performed less than 0.4 minutes, the decomposition reaction is intense due to rapid temperature rise, and thus high-strength carbon fibers may not be obtained. If the processing time exceeds 2.0 minutes, the influence on the plasticization in the early stage of the process is occurred, and thus the crystal orientation tends to decrease. As a result, the mechanical performance of the resulting carbon fibers is impaired. The processing time is more preferably 0.6 to 1.8 minutes.

[0080] Next, a heat treatment is performed under tension in a second carbonization furnace that has a temperature gradient of 1000° C. to 2400° C. in an inert atmosphere, such as nitrogen, so as to obtain a carbon fiber bundle.

[0081] The temperature of the second carbonization furnace is set according to the balance of the strength and the elastic modulus of the desired carbon fibers. The temperature of the second carbonization furnace may be 1000° C. or more, and more preferably 1050° C. or more. The temperature gradient is not particularly limited, but it is preferable to raise the temperature linearly with the temperature gradient being substantially constant. The processing time is preferably 0.4 to 3.0 minutes, and more preferably 0.6 to 2.0 minutes. In this process, due to the large shrinking tendency of the fiber bundle, it is important to perform the heat treatment with tension. The stretching is preferably -10.0% to 2.0%. In the case where the stretching is less than -10.0% (shrinkage of more than 10%), the crystal has a poor orientation in the fiber axial direction and sufficient performance is not achieved. On the other hand, if the stretching exceeds 2.0%, the structure that has been formed so far is seriously damaged and formation of defects becomes noticeable, and thus the strength decreases significantly. A more preferable stretching range is -7.0% to 0.0%.

[Surface Treatment]

[0082] Surface treatment is performed on the fiber bundle that has been carbonized. The surface treatment method includes the conventional method for producing carbon fibers with general fineness, i.e. oxidation methods by electrolytic oxidation, agent oxidation, and air oxidation, for example. Electrolytic oxidation is preferable for it may achieve stable surface oxidation treatment.

[0083] In order to control a preferable surface treated condition, the quantity of electricity is controlled in the electrolytic oxidation process. In this case, even with the same quantity of electricity, the surface treated condition may differ significantly according to the electrolyte used and its concentration. However, in an alkaline aqueous solution, it is preferred to perform the oxidation by using the carbon fiber bundle as the anode and supplying a quantity of electricity of 10 to 1000 coulomb/g. Regarding the electrolyte, it is preferable to use ammonium carbonate, ammonium bicarbonate, calcium hydroxide, sodium hydroxide, potassium hydroxide, etc.

[Sizing Process]

[0084] A sizing process is performed on the fiber bundle that has been surface-treated. The sizing agent may be applied by applying a solution obtained by dissolving a compound, such as a resin, in an organic solvent, or an emulsion liquid obtained by dispersing an emulsifier or the like in water to the fiber bundle by an immersion method or a roller contact method, and then the solvent or the water is dried. The amount of the sizing agent applied to the surface of the carbon fibers may be adjusted through concentration adjustment or squeeze amount adjustment of the sizing agent solution or dispersion. Furthermore, the drying may be performed by using hot air, a hot plate, a heating roller, and various infrared heaters, for example.

[Sizing Agent Composition]

[0085] The sizing agent composition is not particularly limited. For example, a urethane modified epoxy resin including

a urethane bond unit having a polyhydroxy compound and a diisocyanate structure containing an aromatic ring and an epoxy group may be used as the sizing agent composition. The sizing agent composition is a compound that can adhere strongly to the carbon fiber surface and has flexibility, and a flexible interface layer strongly adhering to the carbon fiber surface may be formed by the composite process of impregnating and curing matrix resin. Consequently, the carbon fiber processed with such a sizing agent composition is excellent in attaining mechanical performance of the composite material.

[Merger of Fiber Bundles]

[0086] When the ultrafine fiber bundle is for industrial use, the total fineness of the bundle is preferably to be large. However, in the spinning process, it is difficult to produce a large fiber bundle having the total fineness as described above. Thus, in any process after the spinning, it is preferable to merge a plurality of fiber bundles. It is preferred to perform the merging after the stabilization processing.

[Evaluation of Strand Performance of Carbon Fiber Bundle]

[0087] Preparation of a strand sample of the resin-impregnated carbon fiber bundle and measurement of the strength are carried out in compliance with JIS R7608. Moreover, calculation of the elastic modulus is performed according to Method A of the same standard.

[Method of Measuring Graphite Crystallite Size Lc]

[0088] The graphite crystallite size Lc of the carbon fibers may be obtained by the following method. (1) The carbon fiber bundle to be used for the measurement is cut into a length of 50 mm, and 12 mg of which is accurately weighed and collected. The single fibers that constitute the fiber bundle are aligned to make the fiber axes thereof parallel to each other, so as to arrange the fiber bundle into a fiber sample bundle having a width of 1 mm and a uniform thickness. (2) Two ends of the fiber sample bundle are impregnated with a vinyl acetate/methanol solution and the fiber sample bundle is fixed such that this form does collapse. Thereafter, the fiber sample bundle is fixed on a wide-angle X-ray diffraction sample stage. (3) A CuK α ray (Ni filter used) X-ray generator (trade name: TTR-III, rotating anode X-ray generator) produced by Rigaku

[0089] Corporation is used as X-ray source. With use of a goniometer manufactured by Rigaku Corporation, a diffraction peak near $2\theta=26^\circ$ corresponding to the plane index d(002) of graphite in the transmission method is detected by a scintillation counter. The measurement is performed with an output of 50 kV-300 mA. Based on the half width of the diffraction peak, the crystal size Lc is determined by using the following equation (3).

$$Lc = K\lambda / (\beta_0 \cos \theta) \quad (3)$$

(in the equation, K is a Scherrer constant which is 0.9, λ is the wavelength of the X-ray used (which is 0.15418 nm since the CuK α ray is used here), θ is a diffraction angle of Bragg, β_0 is the true half width, and $\beta_0 = \beta_E - \beta_1$ (β_E is the apparent half width and β_1 is a device constant, which is 0.063 rad here).

[Method of Measuring Crystal Orientation π of Graphite Crystallite in the Fiber Axial Direction]

[0090] A sample is prepared in the same manner as for the measurement of the graphite crystallite size Lc. At 2θ that

includes the maximum intensity of the d(002) diffraction obtained by the same analysis method, the diffraction intensity is measured while the sample fiber bundle is rotated 360° on a plane perpendicular to the X-ray. Based on the half width (H°) of the diffraction profile, the crystal orientation π (%) is determined by using the following equation (4).

$$\pi = [(180 - H) / 180] \times 100 \quad (4)$$

[0091] Hereinafter, the invention is described specifically with reference to the embodiments below.

EMBODIMENTS

Embodiment 1

[0092] A copolymer obtained by copolymerizing 97 mass % of acrylonitrile, 2 mass % of acrylamide, and 1 mass % of methacrylic acid is dissolved in dimethylacetamide (referred to as DMAc hereinafter), which is then filtered by a sintered metallic filter having a filtration accuracy of 5 μm . The copolymer concentration is 16.0 mass %. This is used as the dope. The viscosity thereof is 80 poise at 50° C.

[0093] The dope is discharged into a coagulation liquid of 50° C. including 30 mass % of DMAc from a spinning nozzle produced by an electroforming method, wherein the hole density of the spinning nozzle is 1111/mm², the discharge hole diameter is 15 μm , the distance between the edges of the discharge holes is 0.015 mm, the perforate portion width is 1 mm, the distance between the perforate portions is 2 mm, the number of the perforate portions is 30, and the total hole number is 1.17×10^6 . The coagulated threads are stretched 4.4 times while being washed in hot water of 98° C. for removing the DMAc. Then, the coagulated threads are relaxed 0.98 times in hot water of 95° C.

[0094] An oil agent including amino-modified silicone as the main component is applied to the obtained fiber bundle. The fiber bundle is put in contact with hot rollers to be dried. The amount of the oil agent component contained in the fiber bundle is set to 1.5 mass %. The fiber bundle is heated to 170° C. by dry heating and stretched 2.2 times. Here, an aqueous fiber oil agent that includes amino-modified silicone as the main component is the following:

[0095] Amino-modified silicone: KF-865 (produced by Shin-Etsu Chemical Co., Ltd.) 85 mass % (side chain type monoamine-modified type, viscosity 110 cSt (25° C.), and amino equivalent 5,000 g/mol);

[0096] Emulsifier: NIKKOL BL-9EX (produced by Nikko Chemicals Co., Ltd.) 15 mass %.

[0097] By the method described above, a carbon fiber precursor fiber bundle, which has the average single fiber fineness of 0.0062 dtex and the total fineness of 7254 dtex and substantially has no single fiber adhered to each other, may be obtained.

[0098] Next, ten carbon fiber precursor fiber bundles are arranged side by side at a pitch of 1 cm and introduced into a stabilization processing furnace, and air heated to 220° C. to 280° C. is blown to the carbon fiber precursor fiber bundles to perform the stabilization processing to obtain a stabilized fiber bundle having a density of 1.355 g/cm³. The stretching rate is set to -5.0%. The stabilization processing time is 35 minutes.

[0099] Then, the stabilized fiber bundle passes through a first carbonization furnace, which has a temperature gradient set to 300° C. to 700° C. in nitrogen, while stretching of 3.5% is further applied. The temperature gradient is substantially

constant, such that the temperature increases linearly. The processing time is set to 0.8 minutes.

[0100] Further, a heat treatment is performed at a predetermined temperature using a second carbonization furnace that has a temperature gradient set to 1000° C. to 1600° C. in a nitrogen atmosphere, so as to obtain a carbon fiber bundle. The stretching rate is -4.5%. The processing time is set to 0.8 minutes.

[0101] The carbon fiber bundle is passed through an aqueous solution of 10 mass % of ammonium bicarbonate. With the carbon fiber bundle as anode, an electrifying process is performed between the anode and the counter electrode with a quantity of electricity of 30 coulombs per gram of the processed carbon fibers, and then the carbon fiber bundle is washed with warm water of 50° C. and then dried.

[0102] The carbon fiber bundle is applied with 0.8 mass % of a sizing agent (Hydran N320) and then dried to be wound on a bobbin.

[0103] By the method described above, a carbon fiber bundle, which has the single fiber fineness of 0.0035 dtex, the average diameter of 0.51 μm , the strand strength of 5500-6000 MPa, and the strand elastic modulus of 285-295 GPa and includes 1,170,000 single fibers, may be obtained.

[0104] The crystal orientation and Lc of the carbon fiber bundle as measured by a wide-angle X-ray diffraction device are 83.3% and 1.4 nm respectively. These satisfy the following two formulas.

$$77 \leq \pi - 3.8 \times Lc \leq 80 \quad \text{formula (1)}$$

$$3.28 \leq -1.05 \times 10^{15} \times E^2 + 0.0194 \times E - Lc \leq 3.94 \quad \text{formula (2)}$$

Embodiment 2

[0105] A carbon fiber precursor fiber bundle, which has the average single fiber fineness of 0.01 dtex and the total fineness of 11700 dtex and substantially has no single fiber adhered to each other, is obtained by the same method as Embodiment 1 except that the amount of the dope discharged from the nozzle per unit time is changed and further the coagulated threads are stretched 1.15 times in the air and then stretched 3.9 times in an aqueous solution of 65° C. including 25 mass % of DMAc and thereafter washed with hot water of 98° C. instead of being stretched 4.4 times while being washed in hot water of 98° C. for removing the DMAc. Thereby, the carbon fiber bundle, obtained by the same method as Embodiment 1 with the exception that the second carbonization furnace is set to 1400-1600 ° C., has the single fiber fineness of 0.0035 dtex, the average diameter of 0.63 μm , the strand strength of 6200-6700 MPa, and the strand elastic modulus of 350-360 GPa and includes 1,170,000 single fibers.

[0106] The crystal orientation and Lc of the carbon fiber bundle as measured by the wide-angle X-ray diffraction device are 86.2% and 2.0 nm respectively.

Embodiment 3

[0107] A carbon fiber precursor fiber bundle, which has the average single fiber fineness of 0.055 dtex and the total fineness of 64350 dtex and substantially has no fiber adhered to each other, is obtained by the same method as Embodiment 1 except that the amount of the dope discharged from the nozzle per unit time is changed and further the coagulated threads are stretched 1.15 times in the air and then stretched 3.9 times in an aqueous solution of 65° C. including 25 mass % of DMAc and thereafter washed with hot water of 98° C. instead of

being stretched 4.4 times while being washed in hot water of 98° C. for removing the DMAc.

[0108] Thereby, the carbon fiber bundle, obtained by the same method as Embodiment 1, has the single fiber fineness of 0.0035 dtex, the average diameter of 1.5 μm, the strand strength of 6000-6500 MPa, and the strand elastic modulus of 335-340 GPa and includes 1,170,000 single fibers.

[0109] The crystal orientation and Lc of the carbon fiber bundle as measured by the wide-angle X-ray diffraction device are 85.4% and 1.7 nm respectively.

INDUSTRIAL APPLICABILITY

[0110] The invention provides a carbon fiber bundle including 300,000 to 2,500,000 single fibers, which have the single fiber fineness of 0.0035-0.056 dtex and are independent of each other.

What is claimed is:

1. A carbon fiber bundle comprising a plurality of continuous single fibers and satisfying the following (1) to (4):

- (1) a fineness of the single fiber is 0.0035-0.056 dtex;
- (2) a number of the single fibers in one carbon fiber bundle is 300-2500 thousand;
- (3) a strand strength of the carbon fiber bundle is 3000-10000 MPa; and
- (4) a strand elastic modulus of the carbon fiber bundle is 200-400 GPa.

2. The carbon fiber bundle according to claim 1, wherein the single fibers are independent single fibers.

3. The carbon fiber bundle according to claim 1, wherein the fineness of the single fiber is greater than 0.0054 dtex.

4. A polyacrylonitrile-based carbon fiber bundle comprising a plurality of continuous single fibers, a crystal orientation π (%) and a graphite crystal size Lc (nm) of which obtained by a wide-angle X-ray diffraction method satisfy the following formula (1):

$$77 \leq \pi - 3.8 \times Lc \leq 80 \quad \text{formula (1)}$$

5. A polyacrylonitrile-based carbon fiber bundle comprising a plurality of continuous single fibers, a graphite crystal

size Lc (nm) of which obtained by a wide-angle X-ray diffraction method and a strand elastic modulus E (GPa) satisfy the following formula (2):

$$3.28 \leq -1.05 \times 10^{-5} \times E^2 + 0.0194 \times E - Lc \leq 3.94 \quad \text{formula (2)}$$

6. A production method of a carbon fiber bundle, comprising:

preparing a dope by dissolving an acrylonitrile-based polymer in a solvent, wherein the acrylonitrile-based polymer is obtained by copolymerizing 96 mass % or more of acrylonitrile and a monomer, which is selected from a (meth)acrylic acid derivative, an itaconic acid derivative, and a (meth)acrylamide derivative, as a copolymer component;

discharging the dope from a spinneret into a coagulation liquid to coagulate the discharged dope to obtain a coagulated thread, wherein the spinneret comprises a perforate portion with a plurality of discharge holes that are arranged and an imperforate portion without discharge hole, and a discharge hole density of the perforate portion with the discharge holes is 600-1200/mm² and a number of the discharge holes is 300-2500 thousand;

after stretching the coagulated thread 1.0-1.5 times, performing stretch and wash to stretch the coagulated thread to a range of 1.5-6 times in a washing and stretching process comprising 2-10 baths having a temperature in a range of 50-100° C.; applying an oil agent comprising a silicone-based compound as a main component; drying the coagulated thread by passing the coagulated thread through a plurality of heating rollers; and heating the coagulated thread at a temperature of 130-200° C. to stretch the coagulated thread 1.3-7.0 times to obtain a polyacrylonitrile-based carbon fiber precursor fiber bundle having a total stretching ratio of 2-16 times;

heating in an oxidizing atmosphere to perform a stabilization process on the polyacrylonitrile-based carbon fiber precursor fiber bundle; and

heating in an inert atmosphere to carbonize the polyacrylonitrile-based carbon fiber precursor fiber bundle.

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