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(54) **CARBON FIBER BUNDLE AND PRODUCTION METHOD THEREFOR**

(57) In order to provide a carbon fiber bundle excellent in strength, elastic modulus, and process stability when subjected to further processing in spite of having a high total fineness, and a method for producing the carbon fiber bundle, the carbon fiber bundle allows a relationship between a coefficient A obtained from an approximation formula (1) of nonlinearity in a stress σ -strain ε curve in a resin-impregnated strand tensile test in a range of stress of 0 to 3 GPa and an orientation parameter of crystallites Π (%) in wide-angle X-ray diffraction measurement to satisfy a formula (2), an initial elastic modulus of the carbon fiber bundle is 240 to 279 GPa, the number of filaments of the carbon fiber bundle is 24,000 to 72,000, and the carbon fiber bundle is substantially untwisted, in which

$$\varepsilon = A\sigma^2 + B\sigma + C \cdots (1)$$

$$-410 \leq (0.0000832\Pi^2 - 0.0184\Pi + 1.00)/A \leq -310 \cdots (2)$$

where, A, B, and C are coefficients of a quadratic function of the stress σ and the strain ε , and Π is an orientation parameter of crystallites.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a carbon fiber bundle that is excellent in strength, elastic modulus, and process stability when subjected to further processing in spite of having high total fineness, and a method for producing the carbon fiber bundle.

BACKGROUND ART

[0002] Carbon fiber bundles have high specific strength and specific elastic modulus, and thus have been developed as reinforcing fibers for composite materials in a wide range of applications including aerospace applications. Recently, carbon fiber bundles have been developed also in industrial applications such as automobile members and wind power generation. In particular, lightweight properties and rigidity are required in wind power generation, and thus carbon fiber bundles excellent in specific elastic modulus are often used, and in recent years, the demand for carbon fiber bundles for wind power generation has expanded.

[0003] In industrial applications, there is a strong demand for cost reduction, and carbon fiber bundles excellent in productivity and having 24,000 or more filaments are often used. In addition, processability of further processing is regarded as important in producing a carbon fiber-reinforced composites such as a prepreg, a towpreg, an intermediate base material such as a woven fabric or a sheet molding compound (SMC), or a drawing material from a carbon fiber bundle. In order to enhance processability of further processing, it is particularly important that the carbon fiber bundle has less fuzz and excellent fiber spreadability, as well as that the entire carbon fiber bundle or a single fiber of the carbon fiber is not broken when unwound from a bobbin and traveled during a production process and exhibits good process stability.

[0004] Generally, a carbon fiber bundle is produced through a stabilization process of oxidizing, in air at 200 to 300°C, a polyacrylonitrile-based precursor fiber obtained by fiberizing a polyacrylonitrile-based copolymer, a pre-carbonization process of heating the stabilized fiber in inert gas at a maximum temperature of 500 to 1,200°C, and a carbonization process of heating the pre-carbonized fiber in inert gas at a maximum temperature of 1,200 to 3,000°C.

[0005] A technique for producing a carbon fiber for industrial use, the carbon fiber having high strength and high elastic modulus and showing excellent processability of further processing, has been heretofore proposed (Patent Documents 1 to 4). Patent Document 1 discloses a technique in which, in the stabilization treatment of a polyacrylonitrile-based precursor fiber bundle having a total fineness of 40,000 dtex or more, defining the shape and arrangement of a turning roller suppresses twisting of the fiber bundle and stably maintaining the form of the fiber bundle while the precursor fiber bundle travels in an oxidation oven, to suppress yarn break and fuzz during the stabilization process, and further to enable a high-quality carbon fiber bundle to be produced stable. Patent Document 2 discloses a technique of controlling a diameter and a surface state of carbon fiber within specific ranges to improve resin impregnating property and spreadability during molding of a composite material. Patent Document 3 discloses a carbon fiber bundle having a semi-permanent twist and an elastic modulus of 200 GPa or more, and discloses a carbon fiber bundle that is excellent in handleability and processability of further processing as a fiber bundle and has a high effect of reinforcing a fiber-reinforced composite material. Patent Document 4 discloses a carbon fiber bundle capable of providing a high-performance carbon-fiber-reinforced composite material having excellent tensile strength by controlling nonlinearity of a stress σ -strain ε curve in a resin-impregnated strand tensile test within a specific range.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0006]

Patent Document 1: Japanese Patent Laid-open Publication No. 2014-214386
 Patent Document 2: Japanese Patent Laid-open Publication No. 2002-69754
 Patent Document 3: Japanese Patent Laid-open Publication No. 2019-151956
 Patent Document 4: International Publication No. 2016/068034

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

5 [0007] However, the background art has the following problems.

[0008] In Patent Document 1, the effect of suppressing the occurrence of twist and "jumping over the groove" (dropping of fibers from the roller) in the stabilization process is shown by setting the yarn density in the stabilization process to a specific range, but the effect of improving the quality of the obtained carbon fiber bundle is not shown, and the process stability when subjected to further processing cannot be improved.

10 [0009] In Patent Document 2, the resin impregnating property at the time of molding a pressure vessel is improved, and the strength transition ratio of the resulting molding material is improved, but the process stability when the obtained carbon fiber bundle is subjected to further processing is not improved.

[0010] In Patent Document 3, although the handleability can be improved by allowing semi-permanent twists to remain in the carbon fiber bundle, there is no disclosure or suggestion of a specific effect on the process stability when the resulting carbon fiber bundle is subjected to further processing, and there is such a problem that, due to the presence of twists, the orientation of fibers in the resulting carbon-fiber-reinforced composite material is disturbed, and mechanical properties are hardly exhibited.

15 [0011] In Patent Document 4, the nonlinearity of the stress σ -strain ε curve in the resin-impregnated strand tensile test is controlled within a specific range by the control of the heat treatment method in the stabilization process, so that the fracture toughness effective for improving the strength is improved. However, there is no suggestion about the process stability when the carbon fiber bundle having a high total fineness is subjected to further processing, and the initial elastic modulus in the resin-impregnated strand tensile test is as high as 315 GPa, so that improvement of the operability when subjected to further processing cannot be expected. Furthermore, in order to obtain a carbon fiber bundle excellent in productivity, it is effective to treat the carbon fiber bundle by increasing the total fineness of the polyacrylonitrile-based precursor fiber bundle. However, there is a limitation on the heat treatment method of the stabilization process due to thermal runaway or the like, and there is such a problem that it is difficult to stably control the nonlinearity of the stress σ -strain ε curve in the method described in the Patent Document.

20 [0012] As described above, in the prior art, there have been proposed a technique for enhancing mechanical properties of a carbon fiber bundle and a technique for enhancing process stability at the time of producing a carbon fiber bundle, but there is not disclosed a technique capable of suppressing troubles such as fuzz due to abrasion with a roller or guide parts during further processing and breakage occurring over a part or the whole of a carbon fiber bundle in a carbon fiber bundle having a large total fineness. An object of the present invention is to provide a carbon fiber bundle that is excellent in strength, elastic modulus, and process stability when subjected to further processing in spite of having a high total fineness, and that easily exhibits mechanical properties when made into a substantially untwisted carbon-fiber-reinforced composite material, and a method for producing the carbon fiber bundle.

SOLUTIONS TO THE PROBLEMS

40 [0013] In order to achieve the object of the present invention, the present invention mainly has the following configuration.

[0014] That is, the present invention provides a carbon fiber bundle in which a relationship between a coefficient A obtained from an approximation formula (1) of nonlinearity in a stress σ -strain ε curve in a resin-impregnated strand tensile test in a range of stress of 0 to 3 GPa and an orientation parameter of crystallites Π (%) in wide-angle X-ray diffraction measurement satisfies a formula (2), an initial elastic modulus is 240 to 279 GPa, and a number of filaments is 24,000 to 72,000, and the carbon fiber bundle is substantially untwisted.

$$\varepsilon = A\sigma^2 + B\sigma + C \cdots (1)$$

$$-410 \leq (0.0000832\Pi^2 - 0.0184\Pi + 1.00)/A \leq -310 \cdots (2)$$

where, A, B, and C are coefficients of a quadratic function of the stress σ and the strain ε , and Π is an orientation parameter of crystallites.

55 [0015] In addition, the present invention is a method for producing the carbon fiber bundle, the method including:

a stabilization process of heat-treating a substantially untwisted polyacrylonitrile-based precursor fiber bundle having 24,000 to 72,000 filaments at a temperature of 220 to 280°C in an oxidizing atmosphere,

a pre-carbonization process of heat-treating the stabilized fiber bundle obtained in the stabilization process in an inert gas at a maximum temperature of 300 to 1,000°C, and
 a carbonization process of heat-treating the pre-carbonized fiber bundle obtained from the pre-carbonized fiber bundle in an inert gas at a maximum temperature of 1,000 to 1,600 °C,
 in which the stretching ratio in the pre-carbonization process is 1.05 to 1.20, the stretching ratio in the carbonization process is 0.960 to 0.990, and the product of the stretching ratios of the pre-carbonization process and the carbonization process is 1.020 to 1.180,
 in the stabilization process, the polyacrylonitrile-based precursor fiber bundle is subjected to a stepwise heat treatment in a plurality of heat treatment ovens set to different temperatures from each other or in a plurality of heat treatment sections provided in a heat treatment oven and set to different temperatures from each other; in the stabilization process, the temperature of the heat treatment oven or the heat treatment section having the lowest temperature is set to less than 230°C and the temperature of the heat treatment oven or the heat treatment section having the highest temperature is set to 280°C or less.

EFFECTS OF THE INVENTION

[0016] The present invention can provide a carbon fiber bundle that is excellent in strength, elastic modulus, and process stability when subjected to further processing in spite of having a high total fineness, and that easily exhibits mechanical properties when formed into a carbon-fiber-reinforced composite material.

EMBODIMENTS OF THE INVENTION

[0017] In order to achieve such an object, the present invention has the following configuration.

[0018] In the carbon fiber bundle of the present invention, the value of the coefficient A obtained by introducing a stress σ -strain ε curve obtained by measuring the carbon fiber bundle by a resin-impregnated strand tensile test into the following nonlinearity approximation formula (1) satisfies the following formula (2).

$$\varepsilon = A\sigma^2 + B\sigma + C \cdots (1)$$

$$-410 \leq (0.0000832\Pi^2 - 0.0184\Pi + 1.00)/A \leq -310 \cdots (2)$$

[0019] Herein, Π represents the orientation parameter of crystallites (%) determined by measuring the carbon fiber bundle by wide-angle X-ray diffraction measurement. The orientation parameter of crystallites is obtained by a method for measuring the orientation parameter of crystallites Π of the carbon fiber described later.

[0020] The value of the central term of the formula (2) is -410 to -310, preferably -406 to -343, and more preferably -386 to -352.

[0021] In the formula (1), the coefficient A represents nonlinearity of a stress σ -strain ε curve. The coefficient A is obtained by fitting a stress σ -strain ε curve obtained by measuring a carbon fiber bundle by a resin-impregnated strand tensile test to the approximation formula (1) in a stress range of 0 to 3 GPa. As described above, the stress σ -strain ε curve of the carbon fiber bundle generally shows a downward convex curve when the stress σ (GPa) is plotted on the vertical axis and the strain ε (-) is plotted on the horizontal axis, and thus the coefficient A obtained from the approximation formula (1) indicates a negative value. That is, as the coefficient A is closer to 0, the nonlinearity is smaller.

[0022] In addition, the present inventors have found that the correlation with the shear modulus of the carbon fiber is not necessarily sufficient only by the nonlinearity of the stress σ -strain ε curve. Theory related to stress and deformation in carbon fiber is described in, for example, "Carbon" (The Netherlands), Elsevier, 1991, Vol. 29, No. 8, p. 1267-1279, or the like. However, this is an academic study, and is difficult to use for practical studies for controlling the shear modulus of carbon fiber. As a result of repeated studies based on these theories, the present inventors have found that the orientation parameter of crystallites Π , which is relatively easy to measure from a practical viewpoint, and the value $(0.0000832\Pi^2 - 0.0184\Pi + 1.00)/A$ of the central term of the above formula (2) derived from the coefficient A of the above approximation formula (1) has an extremely high correlation with the shear modulus of carbon fiber. More specifically, the shear modulus decreases as the value of the central term of the formula (2) increases, and the shear modulus increases as the value of the central term of the formula (2) decreases.

[0023] The shear modulus is an index of the deformability when stress in the bending or compression direction is applied to a single fiber, and is important for improving process stability in a further processing process. If the value of the central term in the formula (2) is -410 to -310, the fiber is appropriately deformed when subjected to bending or compressive stress in a further processing process, and breakage of the single fiber and subsequent winding of the

single fiber around a roller or guide parts can be suppressed. The coefficient A in the formula (1) can be controlled by the stretching ratio in the stabilization process, the stretching ratio in the pre-carbonization process, and the stretching ratio in the carbonization process. In addition, the orientation parameter of crystallites Π can be controlled by the stretching ratio in the pre-carbonization process, the stretching ratio in the carbonization process, and the temperature in the carbonization process.

[0024] In addition, the carbon fiber bundle of the present invention has an initial elastic modulus of 240 to 279 GPa, preferably 245 to 269 GPa, and more preferably 245 to 260 GPa. The initial elastic modulus is an index of initial deformability when a stress in a tensile direction is applied to a single fiber, and is important for improving process stability in a further processing process. If the initial elastic modulus is 240 to 279 GPa, the fiber is appropriately deformed when subjected to stress in the tensile direction in the further processing process, and breakage of the single fiber and subsequent winding around a roller or guide parts can be suppressed. Such initial elastic modulus is calculated as a reciprocal $1/B$ of a coefficient B when a stress σ -strain ε curve measured by a resin-impregnated strand tensile test described later is fitted by the approximation formula (1). Such initial elastic modulus can be controlled by the stretching ratio in the stabilization process, the stretching ratio in the pre-carbonization process, the stretching ratio in the carbonization process, and the temperature in the carbonization process.

[0025] The carbon fiber bundle of the present invention has 24,000 to 72,000 filaments, preferably 36,000 to 60,000 filaments, and more preferably 48,000 to 50,000 filaments. The number of filaments is the number of the single fiber constituting a carbon fiber bundle; as the number of filaments increases, the productivity of the carbon-fiber-reinforced composite material is excellent. However, when the number of filaments is too large, the mechanical properties of the carbon-fiber-reinforced composite material obtained may be deteriorated due to the spreadability of the carbon fiber bundle and the resin impregnating property. When the number of filaments is 24,000 to 72,000, productivity during composite material molding is excellent, and the composite material can be suitably used for industrial applications. The number of filaments can be controlled by the number of holes of the spinneret as well as by dividing or gathering fibers in the spinning process of the polyacrylonitrile-based precursor fiber bundle.

[0026] The carbon fiber bundle of the present invention is substantially untwisted. The term "substantially untwisted" as used herein means that carbon fiber bundles are twisted 0.5 turns or less per 1 m. If the carbon fiber bundle is substantially untwisted, it is possible to suppress orientation disturbance of fibers in the carbon-fiber-reinforced composite material, and the reinforcing effect of the carbon-fiber-reinforced composite material is improved.

[0027] The carbon fiber bundle of the present invention preferably has a crystallite size L_c of 1.80 to 2.20 nm. The crystallite size L_c is the size in the [002] direction of the crystal of graphite in the carbon fiber. If the crystallite size L_c is 1.80 to 2.20 nm, a carbon fiber more excellent in balance between strength and elastic modulus is obtained. The crystallite size L_c can be evaluated by a method for measuring the crystallite size L_c described later by wide-angle X-ray diffraction measurement. The crystallite size L_c can be controlled by the temperature of the carbonization process.

[0028] The carbon fiber bundle of the present invention has a single fiber fineness of preferably 0.63 to 1.35 dtex, more preferably 0.67 to 1.35 dtex, and still more preferably 0.74 to 1.20 dtex. The single fiber fineness is a mass per unit length of a single fiber. If the single fiber fineness is 0.63 to 1.35 dtex, both productivity and mechanical properties can be achieved. The single fiber fineness can be evaluated by measuring the mass per unit length by the method described later. The single fiber fineness can be controlled by the extrude amount and the stretching ratio for the polyacrylonitrile-based polymer in the spinning process of the polyacrylonitrile-based precursor fiber bundle.

[0029] In the carbon fiber bundle of the present invention, the circularity of a single fiber cross section is preferably 0.86 to 0.98, more preferably 0.87 to 0.96, and still more preferably 0.87 to 0.93. The circularity of the single fiber cross section is defined as follows from the circumferential length L and the area A_{cs} of the single fiber cross section.

$$(\text{Circularity}) = 4\pi A_{cs}/L^2.$$

[0030] If the circularity of the single fiber cross section is 0.86 to 0.98, both the convergency and the abrasion resistance during further processing can be more reliably achieved, and the process stability during further processing is more excellent. The circularity of the single fiber cross section can be evaluated from an image of a cut surface obtained by vertically cutting the single fiber by a method described later. The circularity of the single fiber cross section can be controlled by the shape of the extrude hole of the spinneret in the spinning process and the condition of the coagulation process.

[0031] Then, a method for producing a carbon fiber bundle preferable for obtaining the carbon fiber bundle of the present invention will be described.

[0032] In the production of a carbon fiber bundle, a polyacrylonitrile-based precursor fiber bundle is produced. As a raw material to be provided for the production of the polyacrylonitrile-based precursor fiber bundle, a polyacrylonitrile polymer is preferably used. In the present invention, the polyacrylonitrile polymer refers to a polymer in which at least acrylonitrile is a main constituent of the polymer unit, and the main constituent typically refers to a constituent that

accounts for 90 to 100% by mass of the polymer unit. The polyacrylonitrile polymer preferably contains a copolymerization component such as itaconic acid, acrylamide, or methacrylic acid from the viewpoint of improving the spinning properties and from the viewpoint of efficiently performing the stabilization treatment. The method for producing the polyacrylonitrile polymer can be selected from known polymerization methods. In the production of the polyacrylonitrile-based precursor fiber bundle, a spinning dope solution is obtained by dissolving the polyacrylonitrile polymer in a solvent in which polyacrylonitrile is soluble, such as dimethylsulfoxide, dimethylformamide, dimethylacetamide, or an aqueous solution of nitric acid, zinc chloride, or sodium rhodanide.

[0033] The method for producing the polyacrylonitrile-based precursor fiber bundle used in the present invention is not particularly limited, but wet spinning is preferably used, and the polyacrylonitrile-based precursor fiber bundle can be obtained through processes such as stretch, water washing, oil agent application, dry densification, and if necessary, post-stretch. The number of holes of the spinneret in the production process of the polyacrylonitrile-based precursor fiber bundle is preferably 3,000 to 200,000 holes in order to achieve the number of filaments of the carbon fiber bundle described above, and a polyacrylonitrile-based precursor fiber bundle having a predetermined number of filaments can be obtained by dividing or gathering the filaments.

[0034] In the production of the polyacrylonitrile-based precursor fiber bundle, the coagulation bath preferably contains a solvent used as a solvent of the spinning dope solution, such as dimethylsulfoxide, dimethylformamide, and dimethylacetamide, and a so-called coagulant. As the coagulant, a component that does not dissolve a polyacrylonitrile polymer and is compatible with the solvent used in the spinning dope solution can be used. Preferably, water is used as the coagulant.

[0035] In the production of the polyacrylonitrile-based precursor fiber bundle, it is preferable to use a washing bath having a plurality of stages at a temperature of 30 to 98°C in the water washing process. In addition, in the water washing process, the stretching ratio is preferably set to 2 to 6 times.

[0036] After the water washing process, preferably an oil agent of silicone or the like is applied to the yarn for a purpose of preventing adhesion between single fibers. The silicone oil agent is preferably modified silicone, and preferably contains amino-modified silicone having high heat resistance.

[0037] A known method can be used for the dry heat treatment process (the above-described dry densification process). For example, the drying temperature is 100 to 200°C.

[0038] The single fiber fineness of the polyacrylonitrile-based precursor fiber bundle in the method for producing a carbon fiber bundle of the present invention is preferably 1.20 to 2.40 dtex, more preferably 1.20 to 2.20 dtex, and still more preferably 1.40 to 1.80 dtex. The single fiber fineness is a mass per unit length of a single fiber. If the single fiber fineness is 1.20 dtex or more, a carbon fiber bundle is obtained with sufficiently high productivity; if the single fiber fineness is 2.40 dtex or less, treatment unevenness in heat treatment after the stabilization process is reduced, and a carbon fiber bundle having high mechanical properties is obtained. The single fiber fineness can be controlled by the extrude amount and the stretching ratio in the spinning process.

[0039] The polyacrylonitrile-based precursor fiber bundle in the method for producing a carbon fiber bundle of the present invention preferably has a circularity of a single fiber cross section of 0.86 to 0.98, more preferably 0.87 to 0.96, and still more preferably 0.87 to 0.93. The circularity of the single fiber cross section is defined as follows from the circumferential length L and the area A_{cs} of the single fiber cross section.

$$(\text{Circularity}) = 4\pi A_{cs}/L^2.$$

[0040] If the circularity of the single fiber cross section is 0.86 to 0.98, both the convergency and the abrasion resistance of the obtained carbon fiber can be more reliably achieved, and the obtained carbon fiber bundle is more excellent in process stability during further processing. The circularity of a single fiber cross section of the polyacrylonitrile-based precursor fiber bundle can be evaluated from an image of a cut surface obtained by vertically cutting a single fiber by a method described later. The circularity of the single fiber cross section of the polyacrylonitrile-based precursor fiber bundle can be controlled by the shape of the extrude hole of the spinneret in the spinning process and the conditions of the coagulation process.

[0041] The number of filaments of the polyacrylonitrile-based precursor fiber bundle in the method for producing a carbon fiber bundle of the present invention is preferably 24,000 to 72,000, more preferably 36,000 to 60,000, and still more preferably 48,000 to 50,000. The number of filaments is the number of the single fiber constituting the polyacrylonitrile-based precursor fiber bundle; as the number of filaments increases, the productivity of carbon fiber bundle production and the productivity of a carbon-fiber-reinforced composite material with the obtained carbon fiber bundle are excellent. However, if the number of filaments is too large, treatment unevenness in the stabilization process, the pre-carbonization process, and the carbonization process may increase, or the mechanical properties of the carbon-fiber-reinforced composite material obtained from the viewpoint of the spreadability of the obtained carbon fiber bundle and the resin impregnating property may deteriorate. If the number of filaments of the polyacrylonitrile-based precursor

fiber bundle is 24,000 to 72,000, there is obtained a carbon fiber bundle that is excellent in productivity of the carbon fiber bundle and the carbon-fiber-reinforced composite material and that can be suitably used for industrial applications. The number of filaments of the polyacrylonitrile-based precursor fiber bundle can be evaluated by counting the number of single fibers constituting the polyacrylonitrile-based precursor fiber bundle. The number of filaments can be controlled by the number of holes of the spinneret in the spinning process, the partition number of the fiber bundle extruded from the spinneret, and the number of gather of the fiber bundle.

[0042] In the method for producing a carbon fiber bundle of the present invention, the substantially untwisted polyacrylonitrile-based precursor fiber bundle as described above is heat-treated at a temperature of 220 to 280°C in an oxidizing atmosphere (stabilization process). The temperature in the stabilization process is preferably 220 to 280°C. If the temperature of the stabilization treatment is 220°C or more, a stabilized fiber bundle having sufficient flame resistance can be produced, so that generation of fuzz due to insufficient flame resistance can be suppressed, and the obtained carbon fiber bundle is excellent in process stability during further processing. If the temperature at which the stabilization treatment is performed is 280°C or less, the exothermic rate is not excessively increased, so that temperature unevenness in the stabilized fiber bundle can be reduced, and a carbon fiber bundle excellent in mechanical properties can be obtained. The temperature of the stabilization treatment may be measured by inserting a thermometer such as a thermocouple into an oxidation oven, and a simple average temperature is calculated if there is temperature unevenness or temperature distribution when the temperature in the oven is measured at several points. The temperature of the stabilization treatment can be controlled by the output of heating in a heating method used in a known oxidation oven. For example, in the case of a hot air circulation type oxidation oven, the output of the heater used for heating the oxidizing atmosphere may be changed.

[0043] In the stabilization process, the polyacrylonitrile-based precursor fiber bundle is subjected to heat treatment stepwise using a plurality of heat treatment ovens set to different temperatures from each other or a plurality of heat treatment sections provided in a heat treatment oven and set to different temperatures from each other (in the following, such heat treating ovens and sections may be referred to as "heat treating ovens/sections"). In the present invention, the temperature may be different between at least two heat treatment ovens/heat treatment sections among the plurality of heat treatment ovens/heat treatment sections; for example, two heat treatment ovens/heat treatment sections among the three heat treatment ovens/heat treatment sections may have the same temperature. In the present invention, the lowest temperature of the heat treatment oven or the heat treatment section in the stabilization process is set to less than 230°C, preferably 225°C or less, and more preferably 223°C or less. Setting the lowest temperature of the heat treatment oven or heat treatment section to less than 230°C can reduce heat treatment unevenness that is likely to occur in the polyacrylonitrile-based precursor fiber bundle having a high total fineness, and the quality can be maintained high in the stretch of the pre-carbonization process and the carbonization process described later. If the lowest temperature of the heat treatment oven or heat treatment section is 230°C or more, heat treatment unevenness in the stabilization process increases, and the quality is deteriorated by stretch in the pre-carbonization process and the carbonization process.

[0044] In the present invention, the highest temperature of the heat treatment oven or the heat treatment section in the stabilization process is set to 280°C or less, preferably 275°C or less, and more preferably 270°C or less. Setting the highest temperature of the heat treatment oven or heat treatment section to 280°C or less can reduce heat treatment unevenness that is likely to occur in the polyacrylonitrile-based precursor fiber bundle having a high total fineness, and the quality can be maintained high in the stretch of the pre-carbonization process and the carbonization process described later. If the temperature of the heat treatment oven or heat treatment section is more than 280°C, heat treatment unevenness in the stabilization process increases, and the quality is deteriorated by stretch in the pre-carbonization process and the carbonization process.

[0045] The production process of the polyacrylonitrile-based precursor fiber bundle and the stabilization process are followed by pre-carbonization. In the pre-carbonization process, the stabilized fiber bundle obtained as described above is heat-treated in an inert gas at a maximum temperature of 300 to 1,000°C, preferably until the density reaches 1.5 to 1.8 g/cm³.

[0046] The pre-carbonization is followed by carbonization. In the carbonization process, the pre-carbonized fiber bundle is heat-treated in an inert gas at a maximum temperature of 1,000 to 1,600°C.

[0047] In the present invention, also in the pre-carbonization process and the carbonization process, a plurality of heat treatment ovens or heat treatment sections may be used and set to temperatures different from each other. Therefore, the temperature of a heat treatment oven or a heat treatment section having the highest temperature in each process is referred to as a "maximum temperature".

[0048] In the method for producing a carbon fiber bundle of the present invention, the stretching ratio in the pre-carbonization process is 1.05 to 1.20, the stretching ratio in the carbonization process is 0.960 to 0.990, and the product of the stretching ratios in the pre-carbonization process and the carbonization process is 1.020 to 1.180.

[0049] The stretching ratio in the pre-carbonization process is preferably 1.10 to 1.20, and more preferably 1.10 to 1.15.

[0050] The stretching ratio in the carbonization process is preferably 0.975 to 0.990, and more preferably 0.975 to 0.985.

[0051] The product of the stretching ratio in the pre-carbonization process and the stretching ratio in the carbonization process is preferably 1.040 to 1.130 and more preferably 1.070 to 1.130.

[0052] Controlling so that the stretching ratio in the pre-carbonization process is 1.05 or more, the stretching ratio in the carbonization process is 0.960 or more, and the product of the stretching ratio in the pre-carbonization process and the stretching ratio in the carbonization process is 1.020 or more, the value of the central term in the formula (2) and the initial elastic modulus of the obtained carbon fiber bundle can be controlled within appropriate ranges. On the other hand, controlling so that the stretching ratio in the pre-carbonization process is 1.20 or less, the stretching ratio in the carbonization process is 0.990 or less, and the product of the stretching ratio in the pre-carbonization process and the stretching ratio in the carbonization process is 1.180 or less, yarn break due to stretch can be suppressed, and a deterioration in process stability during carbon fiber production and an increase in the number of fuzzes of the obtained carbon fiber bundle can be suppressed.

[0053] The carbon fiber bundle obtained as described above is preferably subjected to an oxidation treatment so that an oxygen containing functional group is introduced, in order to improve adhesion to a matrix resin. As the oxidation treatment method, gas phase oxidation, liquid phase oxidation or liquid phase electrolytic oxidation is used. From the viewpoint that high productivity and uniform treatment can be achieved, liquid phase electrolytic oxidation is preferably used. The method of liquid phase electrolytic oxidation is not particularly specified, and may be performed by a known method.

[0054] After the electrolytic treatment, the obtained carbon fiber bundle can be subjected to sizing treatment for imparting convergency to the carbon fiber bundle. For the sizing agent, a sizing agent well compatible with the matrix resin used in the composite can be appropriately selected according to the type of the matrix resin.

EXAMPLES

[0055] Hereinafter, the present invention will be more specifically described with reference to Examples. However, the present invention is not limited thereto.

<Resin-impregnated strand tensile test of carbon fiber bundle>

[0056] The tensile modulus of resin-impregnated strands of the carbon fiber bundle (tensile modulus of resin-impregnated strands E (GPa)), the tensile strength of resin-impregnated strands (tensile strength of resin-impregnated strands (GPa)), and the stress σ -strain ε curve are determined in accordance with JIS R 7608 (2008) "Resin-impregnated strand test method". The tensile modulus of resin-impregnated strands E of resin-impregnated strands is measured under a strain in the range of 0.1 to 0.6%. The test piece is produced by impregnating the carbon fiber bundle with the following resin composition, and under the curing conditions of heat treatment at a temperature of 130°C for 35 minutes.

[Resin composition]

[0057]

- 3,4-Epoxy cyclohexylmethyl-3,4-epoxy-cyclohexanecarboxylate (100 parts by mass)
- Boron trifluoride monoethylamine (3 parts by mass)
- Acetone (4 parts by mass)

[0058] In addition, the number of strands to be measured is 6, and the arithmetic average value of the measurement results is regarded as the tensile modulus of resin-impregnated strands and the tensile strength of resin-impregnated strands of the carbon fiber bundle.

<Analysis of stress σ -strain ε curve>

[0059] In the analysis of the stress σ -strain ε curve obtained by the resin-impregnated strand tensile test, the strain ε (-) is plotted on the vertical axis and the stress σ (GPa) is plotted on the horizontal axis, and the coefficients A, B, and C were calculated by fitting with the following formula (1). The fitting is performed in a region where the stress σ is 0 to 3 GPa in the stress σ -strain ε curve obtained by the measurement. The fitting is performed by a quadratic function using "Excel" manufactured by Microsoft Corporation.

$$\varepsilon = A\sigma^2 + B\sigma + C \cdots (1) .$$

<Initial elastic modulus (GPa)>

[0060] The initial elastic modulus of the carbon fiber bundle is calculated as follows by analysis of the stress σ -strain ε curve described above using the coefficient B obtained by fitting with the formula (1).

$$\text{Initial elastic modulus (GPa)} = 1/B.$$

<Orientation parameter of crystallites Π (%) for carbon fiber bundle>

[0061] Carbon fiber bundles to be measured are aligned and solidified using a collodion alcohol solution to prepare a quadrangular prism measurement sample having a length of 4 cm and a side length of 1 mm. The prepared measurement sample is measured under the following conditions using a wide-angle X-ray diffractometer.

- X-ray source: $\text{CuK}\alpha$ ray (tube voltage 40 kV, tube current 30 mA)
- Detector: goniometer + monochromator + scintillation counter

[0062] A peak appearing in the vicinity of $2\theta = 25^\circ$ to 26° is obtained using the following formula from the half width H ($^\circ$) of the diffraction intensity distribution obtained by scanning the peak in the circumferential direction.

$$\text{Orientation parameter of crystallites } \Pi \text{ (\%)} = [(180 - H)/180] \times 100$$

[0063] In examples, XRD-6100 manufactured by Shimadzu Corporation was used as the wide-angle X-ray diffractometer.

<Crystallite size L_c (nm)>

[0064]

- X-ray source: $\text{CuK}\alpha$ ray (tube voltage 40 kV, tube current 30 mA)
- Detector: goniometer + monochromator + scintillation counter
- Scanning range: $2\theta = 10$ to 40°
- Scanning mode: step scan, step unit 0.02° , counting time 2 seconds.

[0065] In the obtained diffraction pattern, a half-value width is obtained for a peak appearing in the vicinity of $2\theta = 25$ to 26° , and the crystallite size is calculated from this value by the following Scherrer formula.

$$\text{Crystallite size (nm)} = K\lambda/\beta_0 \cos\theta_B$$

where

- K: 1.0, λ : 0.15418 nm (wavelength of X-ray)
- β_0 : $(\beta_E^2 - \beta_1^2)^{1/2}$
- β_E : apparent half-value width (measured value) rad
- β_1 : 1.046×10^{-2} rad
- θ_B : diffraction angle of Bragg

<Measurement of circularity (-)>

[0066] The polyacrylonitrile-based precursor fiber bundle or the carbon fiber bundle is cut with a single-edged razor perpendicular to the fiber axis direction, and the obtained cross section is observed from the direction perpendicular to the fiber cross section using a scanning electron microscope (SEM) "S-4800" manufactured by Hitachi High-Technologies Corporation. The acquired image is analyzed using image analysis software "ImageJ", and for a single fiber included in the fiber cross section, the circularity is calculated from the circumferential length and area of the cross section of the single fiber according to the following definition. This measurement is repeated for 25 single fibers at random in one cross section, and the average of the circularity is regarded as the circularity of the single fiber cross section.

[0067] The circularity of the single fiber cross section is defined as follows from the circumferential length L and the area A_{cs} of the single fiber cross section.

$$(\text{Circularity}) = 4\pi A_{cs}/L^2.$$

<Evaluation of processability of further processing>

[0068] A bobbin of the carbon fiber bundle is set on a creel, drawn out at a tension of 1.6 mN/dtex through 10 free rollers, rubbed against 5 fixed guide parts, taken up by a drive roller at a speed of 10 m/min, and wound up by a winder. At this time, the generated fuzz is counted for 10 minutes immediately before the driving roller, and evaluated by the following indices.

A: less than 10/m

B: 10/m or more and less than 50/m

C: 50/m or more.

(Examples 1 to 4)

[0069] A polyacrylonitrile-based copolymer of acrylonitrile and itaconic acid was polymerized by a solution polymerization method using dimethyl sulfoxide as a solvent to produce a polyacrylonitrile-based copolymer, thereby providing a spinning dope solution. The obtained spinning dope solution was coagulated by a wet spinning method of being introduced into a coagulation bath of an aqueous solution of dimethyl sulfoxide from a spinneret having 50,000 holes to form a fiber bundle. This fiber bundle was washed with water at 30 to 98°C by a conventional method, and stretched at that time. Subsequently, an amino-modified silicone oil agent was applied to the fiber bundle after water washing and stretching, and dry densification was performed using a heating roller at 130°C to provide a polyacrylonitrile-based precursor fiber bundle having the number of single fibers of 50,000 and a single fiber fineness of 1.50 dtex. The polyacrylonitrile-based precursor fiber bundle was not twisted.

[0070] The obtained polyacrylonitrile-based precursor fiber bundle was treated in a stabilization process, a pre-carbonization process, and a carbonization process under the conditions shown in Table 1 to provide a carbon fiber bundle. In each of the stabilization process, the pre-carbonization process, and the carbonization process, heat treatment was performed by gradually increasing the temperature by a plurality of heat treatment ovens having different temperatures. The twisting treatment was not performed in the stabilization process, the pre-carbonization process, and the carbonization process. Physical properties of the obtained carbon fiber bundle are shown in Table 2.

(Example 5)

[0071] The same procedures as in Example 1 were performed except that the extrude amount of the spinning dope solution was changed to obtain a polyacrylonitrile-based precursor fiber bundle having a single fiber fineness of 1.65 dtex, and the conditions of the subsequent pre-carbonization process and carbonization process were changed as shown in Table 1.

(Example 6)

[0072] The same procedures as in Example 1 were performed except that the extrude amount of the spinning dope solution was changed to obtain a polyacrylonitrile-based precursor fiber bundle having a single fiber fineness of 2.40 dtex, and the conditions of the subsequent pre-carbonization process and carbonization process were changed as shown in Table 1.

(Example 7)

[0073] The same procedures as in Example 1 were performed except that the stabilization temperature, the stretching ratio in the pre-carbonization process, and the stretching ratio in the carbonization process were changed to the conditions shown in Table 1.

(Comparative Example 1)

[0074] A carbon fiber bundle was obtained in the same manner as in Example 1 except that the stretching ratio in the

pre-carbonization process was changed to 1.00, the stretching ratio in the carbonization process was changed to 0.960, and the product of the stretching ratios was changed to 0.960. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -307, the initial elastic modulus was 213 GPa, and the process stability during further processing was poor.

(Comparative Example 2)

[0075] A carbon fiber bundle was obtained in the same manner as in Example 1 except that the stretching ratio in the pre-carbonization process was changed to 1.01, the stretching ratio in the carbonization process was changed to 0.955, and the product of the stretching ratios was changed to 0.965. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -286, the initial elastic modulus was 215 GPa, and the process stability during further processing was poor.

(Comparative Example 3)

[0076] A carbon fiber bundle was obtained in the same manner as in Example 1 except that the stretching ratio in the pre-carbonization process was changed to 1.02, the stretching ratio in the carbonization process was changed to 0.950, and the product of the stretching ratios was changed to 0.969. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -287, the initial elastic modulus was 220 GPa, and the process stability during further processing was poor.

(Comparative Example 4)

[0077] A carbon fiber bundle was obtained in the same manner as in Example 1 except that the extrude amount of the spinning dope solution was changed to obtain a polyacrylonitrile-based precursor fiber bundle having a single fiber fineness of 0.80 dtex, and the stretching ratio in the pre-carbonization process was changed to 1.05, the stretching ratio in the carbonization process was changed to 0.950, and the product of the stretching ratios was changed to 0.998. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -290, the initial elastic modulus was 218 GPa, and the process stability during further processing was poor.

(Comparative Example 5)

[0078] A carbon fiber bundle was obtained in the same manner as in Example 1 except that the extrude amount of the spinning dope solution was changed to obtain a polyacrylonitrile-based precursor fiber bundle having a single fiber fineness of 3.00 dtex, and the stretching ratio in the pre-carbonization process was changed to 1.00, the stretching ratio in the carbonization process was changed to 0.955, and the product of the stretching ratios was changed to 0.955. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -277, the initial elastic modulus was 225 GPa, and the process stability during further processing was poor.

(Comparative Example 6)

[0079] A polyacrylonitrile-based precursor fiber bundle was obtained in the same manner as in Example 1 except that the spinning dope solution was coagulated by a dry-jet wet spinning method in which the spinning dope solution was once extruded into the air and then introduced into a coagulation bath of an aqueous solution of dimethyl sulfoxide, and a carbon fiber bundle was obtained in the same manner as in Example 1 except that the stretching ratio of the pre-carbonization process was changed to 1.01, the stretching ratio of the carbonization process was changed to 0.965, and the product of the stretching ratios was changed to 0.975. The value of the central term in the formula (2) of the obtained carbon fiber bundle was -290, the initial elastic modulus was 223 GPa, and the process stability during further processing was poor.

(Comparative Example 7)

[0080] The procedure was similar to that in Example 1 except that the stretching ratio in the pre-carbonization process was changed to 1.23; as a result, the fiber bundle was broken in the pre-carbonization process, and a carbon fiber bundle was not obtained.

(Comparative Example 8)

[0081] The procedure was similar to that in Example 1 except that the stretching ratio in the pre-monocarbonization process was controlled to be 1.05, the stretching ratio in the carbonization process was controlled to be 1.000, and the product of the stretching ratios was controlled to be 1.050; the fiber bundle was broken in the carbonization process, and a carbon fiber bundle was not obtained.

(Comparative Example 9)

[0082] The procedure was similar to that in the same manner as in Example 1 except that the temperature of the stabilization process was changed to the conditions shown in Table 1 and the stretching ratio of the pre-carbonization process was set to 1.05; the fuzz of the pre-carbonized fiber bundle was increased and the quality was significantly deteriorated, so that the operation of the subsequent process was not able to be performed and a carbon fiber bundle was not obtained.

(Comparative Example 10)

[0083] The procedure was similar to that in the same manner as in Example 1 except that the temperature of the stabilization process was changed to the conditions shown in Table 1 and the stretching ratio of the pre-carbonization process was set to 1.05; the fuzz of the pre-carbonized fiber bundle was increased and the quality was significantly deteriorated, so that the operation of the subsequent process was not able to be performed and a carbon fiber bundle was not obtained.

[Table 1]

[0084]

[Table 1]

Polyacrylonitrile-based precursor fiber bundle				Production conditions of stabilization, pre-carbonization, and carbonization						
	Number of filaments	Single fiber fineness	Circularity	Minimum temperature for stabilization	Maximum temperature for stabilization	Maximum temperature for pre-carbonization	Maximum temperature for carbonization	Stretching ratio in pre-carbonization process	Stretching ratio in carbonization process	Product of stretching ratios of pre-carbonization process and carbonization process
	number	dtex	-	°C	°C	°C	°C	-	-	-
Example 1	50,000	1.50	0.90	220	260	700	1,400	1.16	0.985	1.143
Example 2	50,000	1.50	0.90	220	260	700	1,400	1.20	0.965	1.158
Example 3	50,000	1.50	0.90	220	260	700	1,400	1.08	0.975	1.053
Example 4	50,000	1.50	0.90	220	260	700	1,400	1.15	0.980	1.127
Example 5	50,000	1.65	0.90	220	260	700	1,400	1.10	0.983	1.081
Example 6	50,000	2.40	0.90	220	260	700	1,400	1.14	0.985	1.123
Example 7	50,000	1.50	0.90	225	250	700	1,400	1.15	0.975	1.121
Comparative Example 1	50,000	1.50	0.90	220	260	700	1,400	1.00	0.960	0.960
Comparative Example 2	50,000	1.50	0.90	220	260	700	1,400	1.01	0.955	0.965
Comparative Example 3	50,000	1.50	0.90	220	260	700	1,400	1.02	0.950	0.969
Comparative Example 4	50,000	0.80	0.90	220	260	700	1,400	1.05	0.950	0.998
Comparative Example 5	50,000	3.00	0.90	220	260	700	1,400	1.00	0.955	0.955
Comparative Example 6	50,000	1.50	1.00	220	260	700	1,400	1.01	0.965	0.975
Comparative Example 7	50,000	1.50	0.90	220	260	700	-	1.23	-	-

(continued)

	Polyacrylonitrile-based precursor fiber bundle			Production conditions of stabilization, pre-carbonization, and carbonization						
	Number of filaments	Single fiber fineness	Circularity	Minimum temperature for stabilization	Maximum temperature for stabilization	Maximum temperature for pre-carbonization	Maximum temperature for carbonization	Stretching ratio in pre-carbonization process	Stretching ratio in carbonization process	Product of stretching ratios of pre-carbonization process and carbonization process
Comparative Example 8	number	dtex	-	°C	°C	°C	°C	-	-	-
	50,000	1.50	0.90	220	260	700	1,400	1.05	1.000	1.050
	50,000	1.50	0.90	235	285	700	-	1.05	-	-
	50,000	1.50	0.90	240	260	700	-	1.05	-	-

[Table 2]

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[0085]

[Table 2]

	Carbon fiber bundle									
	Number of filaments	Single fiber fineness	Circularity	Orientation parameter of crystallites	Coefficient A	Middle term of formula (2)	Initial elastic modulus	Processability of further processing	Tensile strength of resin-impregnated strands	Tensile modulus of resin-impregnated strands
	number	dtex	-	%	-	-	GPa	-	GPa	GPa
Example 1	50,000	0.66	0.90	82.3	-1.22E-04	-402	269	B	4.6	291
Example 2	50,000	0.65	0.90	81.8	-1.27E-04	-406	261	B	4.5	289
Example 3	50,000	0.71	0.90	82.4	-1.43E-04	-343	245	B	4.4	266
Example 4	50,000	0.67	0.90	82.5	-1.28E-04	-376	257	A	4.4	281
Example 5	50,000	0.76	0.90	82.1	-1.43E-04	-352	245	A	4.4	266
Example 6	50,000	1.07	0.90	79.9	-1.58E-04	-386	250	A	4.1	263
Example 7	50,000	0.66	0.90	82.2	-1.31E-04	-379	255	A	4.1	268
Comparative Example 1	50,000	0.78	0.90	81.2	-1.78E-04	-307	213	C	3.8	234
Comparative Example 2	50,000	0.78	0.90	81.3	-1.89E-04	-286	215	C	4.0	235
Comparative Example 3	50,000	0.77	0.90	81.0	-1.93E-04	-287	220	C	4.0	240
Comparative Example 4	50,000	0.40	0.90	81.2	-1.88E-04	-290	218	C	4.0	234
Comparative Example 5	50,000	1.57	0.90	81.6	-1.90E-04	-277	225	C	4.1	240
Comparative Example 6	50,000	0.77	1.00	80.5	-2.00E-04	-290	223	C	4.0	238
Comparative Example 7	50,000	-	-	-	-	-	-	-	-	-

(continued)

	Carbon fiber bundle									
	Number of filaments	Single fiber fineness	Circularity	Orientation parameter of crystallites	Coefficient A	Middle term of formula (2)	Initial elastic modulus	Processability of further processing	Tensile strength of resin-impregnated strands	Tensile modulus of resin-impregnated strands
	number	dtex	-	%	-	-	GPa	-	GPa	GPa
Comparative Example 8	50,000	-	-	-	-	-	-	-	-	-
Comparative Example 9	50,000	-	-	-	-	-	-	-	-	-
Comparative Example 10	50,000	-	-	-	-	-	-	-	-	-

Claims

1. A carbon fiber bundle that allows a relationship between a coefficient A obtained from an approximation formula (1) of nonlinearity in a stress σ -strain ε curve in a resin-impregnated strand tensile test in a range of stress of 0 to 3 GPa and an orientation parameter of crystallites Π (%) in wide-angle X-ray diffraction measurement to satisfy a formula (2), an initial elastic modulus of the carbon fiber bundle being 240 to 279 GPa, a number of filaments of the carbon fiber bundle being 24,000 to 72,000, the carbon fiber bundle being substantially untwisted, in which

$$\varepsilon = A\sigma^2 + B\sigma + C \cdots (1)$$

$$-410 \leq (0.0000832\Pi^2 - 0.0184\Pi + 1.00)/A \leq -310 \cdots (2)$$

where, A, B, and C are coefficients of a quadratic function of stress σ and strain ε , and Π is an orientation parameter of crystallites.

2. The carbon fiber bundle according to claim 1, a single fiber fineness of the carbon fiber bundle being 0.63 to 1.35 dtex.
3. The carbon fiber bundle according to claim 1 or 2, a circularity of a single fiber cross section of the carbon fiber bundle being 0.86 to 0.98.

4. A method for producing the carbon fiber bundle according to any one of claims 1 to 3, the method comprising:

a stabilization process of heat-treating a substantially untwisted polyacrylonitrile-based precursor fiber bundle having 24,000 to 72,000 filaments at a temperature of 220 to 280°C in an oxidizing atmosphere;
 a pre-carbonization process of heat-treating the stabilized fiber bundle obtained in the stabilization process in an inert gas at a maximum temperature of 300 to 1,000°C; and
 a carbonization process of heat-treating the pre-carbonized fiber bundle obtained from the pre-carbonized fiber bundle in an inert gas at a maximum temperature of 1,000 to 1,600 °C,
 wherein a stretching ratio in the pre-carbonization process is 1.05 to 1.20, a stretching ratio in the carbonization process is 0.960 to 0.990, and a product of the stretching ratios of the pre-carbonization process and the carbonization process is 1.020 to 1.180,
 in the stabilization process, the polyacrylonitrile-based precursor fiber bundle is subjected to a stepwise heat treatment in a plurality of heat treatment ovens set to different temperatures from each other or in a plurality of heat treatment sections provided in a heat treatment oven and set to different temperatures from each other;
 in the stabilization process, the temperature of the heat treatment oven or the heat treatment section having the lowest temperature is set to less than 230°C and the temperature of the heat treatment oven or the heat treatment section having the highest temperature is set to 280°C or less.

5. The method for producing a carbon fiber bundle according to claim 4, wherein a single fiber fineness of the polyacrylonitrile-based precursor fiber bundle is 1.20 to 2.40 dtex.
6. The method for producing a carbon fiber bundle according to claim 4 or 5, wherein a circularity of a single fiber cross section of the polyacrylonitrile-based precursor fiber bundle is 0.86 to 0.98.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/042352

A. CLASSIFICATION OF SUBJECT MATTER <i>D01F 9/22</i> (2006.01)i FI: D01F9/22 According to International Patent Classification (IPC) or to both national classification and IPC																								
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D01F9/08-9/32 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2023 Registered utility model specifications of Japan 1996-2023 Published registered utility model applications of Japan 1994-2023 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																								
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>WO 87/02391 A1 (MITSUBISHI RAYON CO., LTD.) 23 April 1987 (1987-04-23) example 2</td> <td>1-6</td> </tr> <tr> <td>Y</td> <td>JP 2005-60871 A (MITSUBISHI RAYON CO., LTD.) 10 March 2005 (2005-03-10) claims, examples</td> <td>1-6</td> </tr> <tr> <td>Y</td> <td>WO 2017/204026 A1 (TORAY INDUSTRIES, INC.) 30 November 2017 (2017-11-30) claims, examples</td> <td>1-6</td> </tr> <tr> <td>Y</td> <td>WO 2019/087766 A1 (TORAY INDUSTRIES, INC.) 09 May 2019 (2019-05-09) claims, examples</td> <td>1-6</td> </tr> <tr> <td>Y</td> <td>JP 2013-181264 A (MITSUBISHI RAYON CO., LTD.) 12 September 2013 (2013-09-12) claims, examples</td> <td>3, 6</td> </tr> <tr> <td>Y</td> <td>JP 2018-145541 A (MITSUBISHI CHEMICAL CORP.) 20 September 2018 (2018-09-20) claims, examples</td> <td>3, 6</td> </tr> <tr> <td>A</td> <td>WO 2016/068034 A1 (TORAY INDUSTRIES, INC.) 06 May 2016 (2016-05-06) claims, examples</td> <td>1-6</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	WO 87/02391 A1 (MITSUBISHI RAYON CO., LTD.) 23 April 1987 (1987-04-23) example 2	1-6	Y	JP 2005-60871 A (MITSUBISHI RAYON CO., LTD.) 10 March 2005 (2005-03-10) claims, examples	1-6	Y	WO 2017/204026 A1 (TORAY INDUSTRIES, INC.) 30 November 2017 (2017-11-30) claims, examples	1-6	Y	WO 2019/087766 A1 (TORAY INDUSTRIES, INC.) 09 May 2019 (2019-05-09) claims, examples	1-6	Y	JP 2013-181264 A (MITSUBISHI RAYON CO., LTD.) 12 September 2013 (2013-09-12) claims, examples	3, 6	Y	JP 2018-145541 A (MITSUBISHI CHEMICAL CORP.) 20 September 2018 (2018-09-20) claims, examples	3, 6	A	WO 2016/068034 A1 (TORAY INDUSTRIES, INC.) 06 May 2016 (2016-05-06) claims, examples	1-6
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