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(54) **POLYACRYLONITRILE PRE-OXIDIZED FIBER, PREPARATION METHOD THEREFOR AND USE THEREOF**

(57) The present disclosure discloses a polyacrylonitrile-based pre-oxidized fiber and its preparation method and application. The polyacrylonitrile-based pre-oxidized fiber comprises a core and a shell wrapping the core, wherein the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter of 475.0-580.0 cN/μm. Polyacrylonitrile-based carbon fibers prepared from the polyacrylonitrile-based pre-oxidized fibers may have reduced or eliminated chemical defects and structural defects, thereby improving the mechanical properties of the carbon fibers.



Fig. 1

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Description**Technical Field**

5 **[0001]** The present disclosure relates to polyacrylonitrile-based fibers, particularly to polyacrylonitrile-based pre-oxidized fibers and their preparation method and application, and also to polyacrylonitrile-based carbon fibers and their preparation method.

Background

10 **[0002]** High-strength and high-modulus polyacrylonitrile (PAN)-based carbon fibers have a variety of excellent properties. Accordingly, they are widely used in various fields, especially in high-end fields such as aerospace and the like. The excellent properties of high-strength and high-modulus polyacrylonitrile (PAN)-based carbon fibers may be reflected in the following three aspects: (1) High-strength and high-modulus polyacrylonitrile-based carbon fibers may be used to form composite materials with high stiffness. In general, unidirectional composite materials prepared from high-strength and high-modulus polyacrylonitrile-based carbon fibers may have a specific modulus of 5-7 times greater than that of aluminum alloy. (2) Polyacrylonitrile-based high-strength and high-modulus carbon fibers may be used to form composite materials with good dimensional stability. For example, by using high-strength and high-modulus polyacrylonitrile-based carbon fibers as reinforcement materials, together with a reasonable lay-up design, composite materials with an almost zero thermal expansion coefficient may be obtained, which have excellent dimensional stability in environments switching between high and low temperatures. (3) Composite materials prepared from high-strength and high-modulus carbon fibers may have a significant weight-reduction effect.

25 **[0003]** Generally, a method for preparing polyacrylonitrile-based carbon fibers may comprise steps of: preparing polyacrylonitrile-based precursor fibers; pre-oxidizing the polyacrylonitrile-based precursor fibers to obtain polyacrylonitrile-based pre-oxidized fibers; carbonizing and graphitizing the polyacrylonitrile-based pre-oxidized fibers to obtain polyacrylonitrile-based carbon fibers. Polyacrylonitrile-based precursor fibers may have a straight and long molecular chain structure. Such structure may impart polyacrylonitrile-based precursor fibers with poor heat resistance, making them not suitable for being directly carbonized and graphitized. Therefore, the pre-oxidation step for the polyacrylonitrile-based precursor fibers may play an important role. In the pre-oxidizing, the long and straight chains of polyacrylonitrile molecules in the polyacrylonitrile-based precursor fibers are gradually converted into a "trapezoidal" polymer structure with excellent heat resistance, so that the obtained polyacrylonitrile-based pre-oxidized fibers may have significantly improved heat resistance. In the subsequent step of carbonizing and graphitizing, non-carbon elements in the polyacrylonitrile-based pre-oxidized fibers may be gradually removed by releasing small molecule gases, with the trapezoidal polymer structure forming the prototype of a graphene-like structure, and being gradually linked to finally form a network layer of graphite sheet.

35 **[0004]** Pre-oxidation of the polyacrylonitrile-based precursor fibers is in fact a process in which oxygen diffuses in the radial direction of the polyacrylonitrile-based precursor fibers and undergoes reactions. Accordingly, the pre-oxidizing degree of the polyacrylonitrile-based precursor fibers depends on processing conditions thereof, such as temperature, atmosphere and other factors. During the pre-oxidation process, therefore, the polyacrylonitrile precursor fiber forms the most common and substantially unavoidable "shell-core" structure, which per se constitutes a structural defect of the fiber. Such defect structure may be further inherited by the polyacrylonitrile-based carbon fibers obtained after carbonization and graphitization treatments, thereby adversely affecting the quality of the carbon fibers.

Summary of the invention

45 **[0005]** The present disclosure is to address the problems of chemical defects and structural defects in polyacrylonitrile-based pre-oxidized fibers and polyacrylonitrile-based carbon fibers in the prior art. Provided in the present disclosure is a polyacrylonitrile-based pre-oxidized fiber and its preparation method and application, wherein the polyacrylonitrile-based pre-oxidized fiber may have an appropriate "characteristic tensile parameter", which is advantageous for reducing the formation of structural defects in the pre-oxidizing stage, so that the polyacrylonitrile-based carbon fiber prepared from the polyacrylonitrile-based pre-oxidized fiber may have reduced or eliminated chemical defects and structural defects, thereby improving the mechanical properties of the carbon fiber. Accordingly, also provided in the present disclosure is a polyacrylonitrile-based carbon fiber and its preparation method.

55 **[0006]** In one aspect, provided in the present disclosure is a polyacrylonitrile-based pre-oxidized fiber, comprising a core and a shell wrapping the core, wherein the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter, A , of 475.0-580.0 cN/ μm , wherein the characteristic tensile parameter, A , is represented as formula (1):

$$A = \frac{1000 \times T \cdot S_c}{\eta \cdot d} = \frac{T}{\eta \cdot d}; \quad (1)$$

wherein, in formula (1), A represents the characteristic tensile parameter of the polyacrylonitrile-based pre-oxidized fiber (cN/ μ m), T represents fracture strength of the polyacrylonitrile-based pre-oxidized fiber (cN), η represents a ratio of the radial cross-section area of the shell to the radial cross-section area of the entire polyacrylonitrile-based pre-oxidized fiber, and d represents a diameter of the polyacrylonitrile-based pre-oxidized fiber (μ m).

[0007] In another aspect, provided in the present disclosure is a polyacrylonitrile-based carbon fiber, which is prepared from the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, and has a tensile strength of greater than or equal to 5000 MPa and a tensile modulus of 500-600 GPa.

[0008] In a further aspect, provided in the present disclosure is a method for preparing a polyacrylonitrile-based pre-oxidized fiber, preferably for preparing the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, comprising at least steps of: subjecting a polyacrylonitrile-based precursor fiber to pre-oxidizing in a low temperature section, pre-oxidizing in a medium temperature section and pre-oxidizing in a high temperature section in sequence, to obtain the polyacrylonitrile-based pre-oxidized fiber;

wherein the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and

the pre-oxidizing in the high temperature section are controlled to have a processing parameter, $C_i = \frac{100P_i}{T_i t_i}$, satisfying formula (2):

$$N_{i, \min} \leq C_i \leq N_{i, \max} \quad (2)$$

wherein, i = 1, 2, 3, corresponding to the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section respectively; P_i is the pressure for each pre-oxidizing (Pa); T_i is the temperature for each pre-oxidizing ($^{\circ}$ C); t_i is the time for each pre-oxidizing (min),

wherein, for the pre-oxidizing in the low temperature section, C1 satisfies: $1.0 \leq C_1 \leq 10.0$ (i.e. in the above formula (2), i=1, $N_{1, \min} = 1.0$ and $N_{1, \max} = 10$), preferably $1.90 \leq C_1 \leq 8.33$ (i.e. in the above formula (2), i=1, $N_{1, \min} = 1.90$ and $N_{1, \max} = 8.33$); for the pre-oxidizing in the medium temperature section, C2 satisfies: $0.1 \leq C_2 \leq 2.5$ (i.e. in the above formula (2), i=2, $N_{2, \min} = 0.1$ and $N_{2, \max} = 2.5$), preferably $0.48 \leq C_2 \leq 1.25$ (i.e. in the above formula (2), i=2, $N_{2, \min} = 0.48$ and $N_{2, \max} = 1.25$); and, for the pre-oxidizing in the high temperature section, C3 satisfies: $0.5 \leq C_3 \leq 4.0$ (i.e. in the above formula (2), i=3, $N_{3, \min} = 0.5$ and $N_{3, \max} = 4$), preferably $0.85 \leq C_3 \leq 2.13$ (i.e. in the above formula (2), i=3, $N_{3, \min} = 0.85$ and $N_{3, \max} = 2.13$).

[0009] In yet another aspect, provided in the present disclosure is a polyacrylonitrile-based pre-oxidized fiber obtained by the method in accordance with the present disclosure.

[0010] In a further aspect, provided in the present disclosure is a use of the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure in preparing a carbon fiber.

[0011] In still another aspect, provided in the present disclosure is a method for preparing a polyacrylonitrile-based carbon fiber, comprising steps of: subjecting a polyacrylonitrile-based pre-oxidized fiber to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence, wherein the polyacrylonitrile-based pre-oxidized fiber is the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure or the polyacrylonitrile-based pre-oxidized fiber prepared by the method in accordance with the present disclosure.

[0012] Compared with the prior art, the present disclosure has the following advantages.

(1) The polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure has a characteristic tensile parameter within a specific range. The inventor surprisingly found that the polyacrylonitrile-based pre-oxidized fiber with the characteristic tensile parameter within that range contains fewer structural and chemical defects, and simultaneously has a radial structure with a larger proportion of shell and a more suitable fiber fracture strength. During the pre-oxidizing of the polyacrylonitrile-based precursor fiber, as oxygen diffuses from outside of the precursor fiber to inside thereof and undergoes a thermal oxidation stabilization reaction, a gradient difference on the stabilization degree between the inside and the outside will inevitably be formed, and the proportion of shell will gradually increase. However, in such a situation, most of the ordered structures and the crystalline structure of the polyacrylonitrile molecules in the inside of the precursor fiber will usually be destroyed

to a certain extent, resulting in decrease in crystallinity, molecular cohesion and rigidity in the inside, thereby adversely affecting fracture strength of the obtained polyacrylonitrile-based pre-oxidized fiber. The polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure can achieve not only a high proportion of shell, but also a small loss in fracture strength of the pre-oxidized fiber. It is unexpected as compared to the polyacrylonitrile-based pre-oxidized fiber obtained by the prior art. More importantly, the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure has a more uniform distribution of oxygen in its shell. The uniform distribution of oxygen can be characterized by SEM-EDS. More uniform distribution of oxygen in the shell means that local accumulation of oxygen can be avoided. The more oxygen is taken into the inside of the polyacrylonitrile-based precursor fiber, the more oxygen accumulates in that area. Accordingly, that area becomes denser and thereby the intermolecular force is smaller. In addition, due to excessive oxygen intake, molecules in the inside of the polyacrylonitrile-based precursor fiber may undergo reactions to such a degree that the structures which contribute mechanical properties are reduced. At the same time, it may also prevent the subsequent diffusion of oxygen towards the inside of the precursor fiber. Those adverse effects may make excessive chemical defects and structural defects be concentrated in the outer area of the polyacrylonitrile-based pre-oxidized fiber, resulting in decrease in fracture strength of the whole pre-oxidized fiber. During the pre-oxidizing, the long and straight chains of polyacrylonitrile molecules in the polyacrylonitrile-based precursor fiber are gradually converted into a trapezoidal polymer structure and crosslinked macromolecules. However, in those areas where local accumulation of oxygen occurs, excessive oxygen intake on the molecular chain may cause the trapezoidal polymer structure to release too much small molecule gas containing oxygen, such as CO_2 , H_2O , NO_x , and the like, in the subsequent step of carbonizing, so that the relatively long chain of polyacrylonitrile molecules may be broken and shortened, resulting in too small size of the graphite embryonic structure. Finally, after carbonization and graphitization, it is difficult to obtain a more regular and large graphite platelet structure, and bubble-shaped voids may remain in the fiber structure. They all may become the sites of stress concentration when the obtained carbon fibers are subjected to external loads, resulting in premature fracture and then adversely affecting performances of the carbon fibers. Therefore, when a carbon fiber is prepared from the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, the obtained carbon fiber may have reduced or eliminated chemical defects and structural defects, thereby improving mechanical properties of the carbon fiber.

(2) During the preparation of the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, the range of the processing parameter C_i is controlled, thereby controlling temperature, pressure and time for the pre-oxidizing. The applicant surprisingly found that by controlling the processing parameters, especially in the preferred embodiment, by optimizing the ranges of temperature, pressure and time of pre-oxidizing in each section, it is easier for oxygen to diffuse into the interior of the polyacrylonitrile-based precursor fiber. Accordingly, during the pre-oxidizing, excessive accumulation of oxygen in the outer surface area of the polyacrylonitrile-based precursor fiber is avoided, thereby avoiding chemical defects and structural defects in the polyacrylonitrile-based pre-oxidized fiber, as described above.

Description of the drawings

[0013] The accompanying drawings are included to provide a further understanding of the invention and are a part of this specification, which, together with the following detailed description, illustrate the invention but not to limit the scope thereof. In the drawings,

Fig. 1 shows an optical microscope image of a cross-section of the polyacrylonitrile-based pre-oxidized fiber obtained in Example 16.

Fig. 2 shows an optical microscope image of a cross-section of the polyacrylonitrile-based pre-oxidized fiber obtained in Comparative Example 1.

Fig. 3 shows a scanning electron microscope (SEM) image of a cross-section of the polyacrylonitrile-based pre-oxidized fiber obtained in Example 16, wherein the linear scanning path for the EDS spectrum is marked.

Fig. 4 shows an energy spectrum of the outer region of the shell of the polyacrylonitrile-based pre-oxidized fiber obtained in Example 16.

Fig. 5 shows an energy spectrum of the inner region of the shell of the polyacrylonitrile-based pre-oxidized fiber obtained in Example 16.

Fig. 6 shows an energy spectrum of the core of the polyacrylonitrile-based pre-oxidized fiber obtained in Example 16.

Detailed description

[0014] The present disclosure will be described in detail below based on the accompanying drawings and embodi-

ments. The features and advantages of the present invention will become more apparent through the detailed description.

[0015] It should be understood that any values disclosed herein (including the endpoints in the ranges) are not limited to the precise value, but to encompass values close to those values, for example, all possible values within a range of the precise value $\pm 5\%$. In addition, for ranges of values, it is possible to combine between the endpoints of each of the ranges, between the endpoints of each of the ranges and the individual points, and between the individual points to give one or more new ranges of values as if these ranges of values are specifically disclosed herein.

[0016] Other than in the examples, all values of parameters in this specification are to be understood as being modified in all instances by the term "about" whether or not "about" actually appears before the values.

[0017] In one aspect, provided in the present disclosure is a polyacrylonitrile-based pre-oxidized fiber, comprising a core and a shell wrapping the core, wherein the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter A of 475.0-580.0 cN/ μm , wherein the characteristic tensile parameter A is represented as formula (1):

$$A = \frac{1000 \times T \cdot S_c}{\eta \cdot d} = \frac{T}{\eta \cdot d}; \quad (1)$$

wherein, in formula (1), A represents the characteristic tensile parameter of the polyacrylonitrile-based pre-oxidized fiber (cN/ μm), T represents fracture strength of the polyacrylonitrile-based pre-oxidized fiber (cN), η represents a ratio of the radial cross-section area of the shell to the radial cross-section area of the entire polyacrylonitrile-based pre-oxidized fiber, and d represents a diameter of the polyacrylonitrile-based pre-oxidized fiber (μm).

[0018] In the present disclosure, fracture strength is obtained by testing according to GB/T 14337-2008.

[0019] In the present disclosure, η may be obtained as follows: obtaining an image of a cross-section of a polyacrylonitrile-based pre-oxidized fiber, and calculating the ratio of the cross-section area of the shell to the cross-section area of the entire polyacrylonitrile-based pre-oxidized fiber, wherein the cross-section of the shell is the dark portion on the periphery in the image of the cross-section of the polyacrylonitrile-based pre-oxidized fiber.

[0020] In a preferred embodiment, $1.5\text{cN} \leq T \leq 8.0\text{cN}$, preferably, $2.5\text{cN} \leq T \leq 5.2\text{cN}$.

[0021] In a preferred embodiment, $55\% \leq \eta \leq 95\%$, preferably, $74\% \leq \eta \leq 91\%$, for example, $\eta = 55\%$, 60% , 65% , 70% , 75% , 80% , 85% , 90% or 95% .

[0022] In a preferred embodiment, $5.0 \mu\text{m} \leq d \leq 15.0 \mu\text{m}$, preferably, $7.0 \mu\text{m} \leq d \leq 10.0 \mu\text{m}$, for example, $d = 5.0 \mu\text{m}$, $6.0 \mu\text{m}$, $8.0 \mu\text{m}$, $10.0 \mu\text{m}$, $12.0 \mu\text{m}$, $14.0 \mu\text{m}$ or $15.0 \mu\text{m}$.

[0023] In a preferred embodiment, the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter of 480.0-575.0 cN/ μm , preferably 482.5-571.5 cN/ μm , for example, 480.0 cN/ μm , 490.0 cN/ μm , 500.0 cN/ μm , 510.0 cN/ μm , 520.0 cN/ μm , 530.0 cN/ μm , 540.0 cN/ μm , 550.0 cN/ μm , 560.0 cN/ μm , 570.0 cN/ μm or 575.0 cN/ μm .

[0024] In a preferred embodiment, the oxygen content difference between the outer area and the inner area of the shell of the polyacrylonitrile-based pre-oxidized fiber is 1.5wt%-3.2wt%, preferably 1.8wt%-2.9wt%; preferably, the outer area of the shell of the pre-oxidized fiber has an oxygen content of 9.0wt%-14.0wt%, preferably 10.5wt%-12.0wt%; the inner area of the pre-oxidized fiber has an oxygen content of 9.0wt%-11.5wt%, preferably 9.5wt%-10.2wt%. In the cross-section of the polyacrylonitrile-based pre-oxidized fiber, the shell is roughly annular, with the outermost side thereof being the surface of the pre-oxidized fiber, and the innermost side being connected to the core. There is a midpoint on the radial line segment connecting the innermost and the outermost sides of the shell. The area covering from the outermost side to the midpoint is the outer area of the shell, and the area covering from the midpoint to the innermost side is the inner area of the shell.

[0025] In one variation, the oxygen content difference between any two points in the shell of the polyacrylonitrile-based pre-oxidized fiber is 1.5wt%-3.2wt%, preferably 1.8wt%-2.9wt%.

[0026] The oxygen content difference between the outer area and the inner area of the shell of the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure is relatively small. Preferably, the oxygen content difference between any two points in the shell is relatively small. Accordingly, oxygen is more uniformly distributed in the shell, rather than being locally accumulated. The oxygen content may be measured by SEM-EDS.

[0027] In another aspect, provided in the present disclosure is a polyacrylonitrile-based carbon fiber, which is prepared from the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, and has a tensile strength of greater than or equal to 4000MPa, preferably greater than or equal to 5000MPa, and a tensile modulus of 500-600 GPa, preferably 540-570GPa.

[0028] In one aspect, provided in the present disclosure is a method for preparing a polyacrylonitrile-based pre-oxidized fiber, preferably for preparing the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure, comprising steps of: subjecting a polyacrylonitrile-based precursor fiber to pre-oxidizing in a low temperature section, pre-oxidizing in a medium temperature section and pre-oxidizing in a high temperature section in sequence, to obtain the polyacrylonitrile-based pre-oxidized fiber;

wherein the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section are controlled to have a processing parameter, $Ci = \frac{100P_i}{T_i t_i}$, satisfying formula (2):

$$N_{i, \min} \leq Ci \leq N_{i, \max} \quad (2)$$

wherein, $i = 1, 2, 3$, corresponding to the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section respectively; P_i is the pressure for each pre-oxidizing (Pa); T_i is the temperature for each pre-oxidizing ($^{\circ}\text{C}$); t_i is the time for each pre-oxidizing (min),

wherein, for the pre-oxidizing in the low temperature section, $1.00 \leq C1 \leq 10.00$, preferably $1.90 \leq C1 \leq 8.33$; for the pre-oxidizing in the medium temperature section, $0.10 \leq C2 \leq 2.50$, preferably $0.48 \leq C2 \leq 1.25$; and, for the pre-oxidizing in the high temperature section, $0.50 \leq C3 \leq 4.00$, preferably $0.85 \leq C3 \leq 2.13$.

[0029] In one embodiment, the pre-oxidizing in the low temperature section is operated under conditions of: a temperature T_1 of $200-210^{\circ}\text{C}$; a time t_1 of no more than 10min, preferably 3-5min; a pressure P_1 of 18-55Pa, preferably 20-50Pa. The pre-oxidizing in the medium temperature section is operated under conditions of: a temperature T_2 of $240-250^{\circ}\text{C}$, a time t_2 of 20-35min, preferably 20-25min; a pressure P_2 of 25-65Pa, preferably 30-60Pa. The pre-oxidizing in the high temperature section is operated under conditions of: a temperature T_3 of $245-280^{\circ}\text{C}$, a time t_3 of 15-25min, preferably 15-18min; a pressure P_3 of 35-85Pa, preferably 40-80Pa.

[0030] In one variation, $T_2 = (1.20-1.22) \cdot T_1$, preferably $20^{\circ}\text{C} \leq T_2 - T_1 \leq 50^{\circ}\text{C}$, more preferably $30^{\circ}\text{C} \leq T_2 - T_1 \leq 40^{\circ}\text{C}$; $0^{\circ}\text{C} \leq T_3 - T_2 \leq 20^{\circ}\text{C}$, preferably $5^{\circ}\text{C} \leq T_3 - T_2 \leq 15^{\circ}\text{C}$, more preferably $10^{\circ}\text{C} \leq T_3 - T_2 \leq 15^{\circ}\text{C}$.

[0031] Preferably, for the pre-oxidizing in the low temperature section, in the above formula (2), $N_{1, \min}$ may be, for example, 1.90, 2.00, 2.50, 3.00, 3.50, 4.00, and the like, and $N_{1, \max}$ may be, for example, 8.33, 8.00, 7.50, 7.00, 6.50, 6.00, 5.50, 5.00, and the like; for the pre-oxidizing in the medium temperature section, in the above formula (2), $N_{2, \min}$ may be, for example, 0.48, 0.50, 0.55, 0.60, and the like, and $N_{2, \max}$ may be, for example, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, and the like; and, for the pre-oxidizing in the high temperature section, in the above formula (2), $N_{3, \min}$ may be, for example, 0.85, 0.90, 0.95, 1.00, and the like, and $N_{3, \max}$ can be 2.13, 2.10, 2.05, 2.00, and the like.

[0032] In the method in accordance with the present disclosure, the "polyacrylonitrile-based precursor fiber" may be replaced by a polyacrylonitrile-based precursor fiber bundle. In one embodiment, the polyacrylonitrile-based precursor fiber bundle has a number of fibers of 1-20K, preferably, 3-12K.

[0033] Preferably, the polyacrylonitrile-based precursor fiber may be prepared by dry spinning or wet spinning, preferably by wet spinning. In one embodiment, a method for preparing polyacrylonitrile-based precursor fiber may comprise steps of: mixing acrylonitrile and a comonomer to form a monomer mixture; polymerizing the monomer mixture to obtain polyacrylonitrile; and spinning polyacrylonitrile to obtain the polyacrylonitrile-based precursor fibers. Examples of the comonomer may include acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, itaconic acid, and the like. Steps of the method for preparing may adopt those processing conditions commonly used in the art.

[0034] In one embodiment, the polyacrylonitrile-based precursor fiber may have a diameter of $5.0-15.0\mu\text{m}$, preferably $7.0-11.0\mu\text{m}$. When a polyacrylonitrile-based precursor fiber bundle is used, the polyacrylonitrile-based precursor fiber may have an average diameter of $5.0-15.0\mu\text{m}$, preferably $7.0-11.0\mu\text{m}$.

[0035] In a preferred embodiment, during the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section, the polyacrylonitrile-based precursor fiber may independently have a drafting ratio of 0.80-1.20, preferably 0.90-1.10.

[0036] The polyacrylonitrile-based pre-oxidized fiber prepared by the method in accordance with the present disclosure may have the properties described above with respect to the polyacrylonitrile-based pre-oxidized fiber, which will not be repeated here.

[0037] In one aspect, provided in the present disclosure is a polyacrylonitrile-based pre-oxidized fiber prepared by the method in accordance with the present disclosure.

[0038] In one aspect, provided in the present disclosure is a method for preparing a polyacrylonitrile-based carbon fiber, comprising steps of: subjecting a polyacrylonitrile-based pre-oxidized fiber to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence, wherein the polyacrylonitrile-based pre-oxidized fiber is the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure or the polyacrylonitrile-based pre-oxidized fiber prepared by the method in accordance with the present disclosure.

[0039] There is no special limitation in the present disclosure on the conditions of carbonizing at the low tempera-

ture, the carbonizing at the high temperature and the graphitizing. Those conditions commonly used in the art may be used. In one embodiment, the carbonizing at the low temperature may be operated under conditions of: a temperature of 200-1000°C, a time of 0.5-10min, and a drafting ratio of 0.80-1.20. Preferably, the carbonizing at the low temperature may be operated under conditions of: a temperature of 400-1000°C, a time of 1-4min, and a drafting ratio of 1.00-1.06. More preferably, the carbonizing at the low temperature may be operated in multiple (e.g., 2-8 or 3-6) temperature zones, wherein the subsequent temperature zone is in a temperature higher than that of the preceding temperature zone.

[0040] In one embodiment, the carbonizing at the high temperature may be operated under conditions of: a temperature of 800-1800°C, a time of 0.5-10min, and a drafting ratio of 0.80-1.00. Preferably, the carbonizing at the high temperature may be operated under conditions of: a temperature of 1000-1500°C, a time of 1-4min, and a drafting ratio of 0.96-0.99. More preferably, the carbonizing at the high temperature may be operated in multiple (e.g., 2-8 or 3-6) temperature zones, wherein the subsequent temperature zone is in a temperature higher than that of the preceding temperature zone.

[0041] In one embodiment, the graphitizing may be operated under conditions of: a temperature of 2200-3000°C, a time of 0.2-15min, and a drafting ratio of 0.90-1.50. Preferably, the graphitizing may be operated under conditions of: a temperature of 2500-2700°C, a time of 1-5min, and a drafting ratio of 1.04-1.15.

[0042] In one variation, the method comprises steps of:

(1) subjecting the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure or the polyacrylonitrile-based pre-oxidized fiber prepared by the method in accordance with the present disclosure to carbonizing at a low temperature wherein the carbonizing at the low temperature is operated under conditions of: a temperature of 300-800°C, a time of 1-4min, and a drafting ratio of 1.00-1.06;

(2) subjecting the polyacrylonitrile-based pre-oxidized fiber obtained in step (1) to carbonizing at a high temperature wherein the carbonizing at the high temperature is operated under conditions of: a temperature of 1000-1500°C, a time of 1-4min, and a drafting ratio of 0.96-0.99;

(3) subjecting the polyacrylonitrile-based pre-oxidized fiber obtained in step (2) to graphitizing, wherein the graphitizing is operated under conditions of: a temperature of 2500-2700°C, a time of 1-5 min, and a drafting ratio of 1.04-1.15.

[0043] In one aspect, provided in the present disclosure is a use of the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure in preparing a carbon fiber. Specifically, the polyacrylonitrile-based pre-oxidized fiber is subjected to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence, to obtain a polyacrylonitrile-based carbon fiber. Preferably, the carbonizing at the low temperature may be operated under conditions of: a temperature of 400-1000°C, a time of 0.5-10min, and a drafting ratio of 0.80-1.20. The carbonizing at the high temperature may be operated under conditions of: a temperature of 800-1800°C, a time of 0.5-10min, and a drafting ratio of 0.80-1.02. The graphitizing may be operated under conditions of: a temperature of 2200-3000°C, a time of 0.2-15min, and a drafting ratio of 0.90-1.50.

[0044] The polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure has a characteristic tensile parameter in a specific range, especially has a more uniform oxygen distribution, thereby has reduced or eliminated chemical defects and structural defects. Accordingly, when preparing a polyacrylonitrile-based carbon fiber from the polyacrylonitrile-based pre-oxidized fiber, the obtained carbon fiber may have significantly improved mechanical properties, wherein the tensile strength is greater than or equal to 4000MPa, preferably greater than or equal to 5000MPa, and the tensile modulus is 500-600GPa, preferably 540-570GPa.

Examples

[0045] The invention will be further described with reference to examples, without limiting the scope of the invention thereto.

[0046] The polyacrylonitrile-based precursor fiber used in the examples and comparative examples was a bundle consisting of 6K polyacrylonitrile-based precursor fibers prepared by a conventional method, wherein the polyacrylonitrile-based precursor fiber contained 95.5wt% of acrylonitrile, 3.5wt% of methyl acrylate and 1.0wt% of itaconic acid, and had a fineness of 0.8551d/tex.

[0047] Testing and calculating of parameters:

η and d: The polyacrylonitrile-based pre-oxidized fiber was cut along the radial direction into ultra-thin slices. An optical microscope image thereof was obtained. The average diameter d of the polyacrylonitrile-based pre-oxidized fiber was measured, and the ratio η of the cross-sectional concentric circle area of the shell of the polyacrylonitrile-based pre-oxidized fiber slice (i.e. all portions with a dark contrast) to the cross-sectional concentric

circle area of the entire polyacrylonitrile-based pre-oxidized fiber slice was calculated.

T: The polyacrylonitrile-based pre-oxidized fiber was tested in a form of single fiber according to GB/T 14337-2008 for fracture strength thereof.

Characteristic tensile parameter: By using the obtained T, η and d, the characteristic tensile parameter of the polyacrylonitrile-based pre-oxidized fiber was calculated according to formula (1).

[0048] The oxygen content difference between the outer area and the inner area of the shell of the pre-oxidized fiber, ΔO : the polyacrylonitrile-based pre-oxidized fiber slice was subjected to SEM-EDS for cross-section morphology characterization and energy spectrum analysis of elements in radial direction by using a scanning electron microscope analysis and characterization instrument Merlin from Zeiss. 10 sampling points were selected along the radial direction of the polyacrylonitrile-based pre-oxidized fiber. The area of the oxygen peak obtained at each sampling point was integrated to obtain an oxygen content (wt%) therefor. The average value of the oxygen contents for the sampling points located in the outer area was used as the oxygen content of the outer area, and the average value of the oxygen contents for the sampling points located in the inner area was used as the oxygen content of the inner area, and the oxygen content difference between the outer area and the inner areas of the shell of the pre-oxidized fiber was calculated therefrom.

[0049] Tensile strength and tensile modulus of a polyacrylonitrile-based carbon fiber: the polyacrylonitrile-based carbon fiber was tested in a form of fiber bundle according to the national standard GB/T25749-2011 for mechanical properties, to obtain tensile strength and tensile modulus thereof.

Comparative Example 1

[0050] The polyacrylonitrile-based precursor fiber was subjected to pre-oxidizing in a low temperature section, under conditions of: a temperature of 180°C, a pressure of 15Pa, and a time of 15min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 0.55, and a drafting ratio of 1.03; then pre-oxidizing in a medium temperature section, under conditions of: a temperature of 230°C, a pressure of 20Pa, and a time of 30min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.29, and a drafting ratio of 1.03; finally, pre-oxidizing in a high temperature section, under conditions of: a temperature of 250°C, a pressure of 25Pa, and a time of 20min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 0.50, and a drafting ratio of 1.00, to obtain a PAN pre-oxidized fiber.

[0051] The polyacrylonitrile-based pre-oxidized fiber was subjected to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence under high-purity nitrogen, to obtain a polyacrylonitrile-based carbon fiber. The carbonizing at the low temperature was operated in four temperature zones having temperatures of 320°C-400°C-550°C-700°C, for a total time of 3 min, at a drafting ratio of 1.06; the carbonizing at the high temperature was operated in four temperature zones having temperatures of 1100°C-1200°C-1300°C-1450°C, for a total time of 2 min, at a drafting ratio of 0.96; the graphitizing was operated at a temperature of 2500°C and a drafting ratio of 1.04 for a time of 3min.

[0052] The PAN pre-oxidized fiber and the polyacrylonitrile-based carbon fiber were subjected to testing and calculating of parameters as mentioned above. The results were shown in Table 1.

Comparative Example 2

[0053] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 160°C, a pressure of 20Pa, and a time of 15min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 0.83, and a drafting ratio of 1.03.

Comparative Example 3

[0054] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 160°C, a pressure of 20Pa, and a time of 20min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 0.62, and a drafting ratio of 1.07.

Comparative Example 4

[0055] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 180°C, a pressure of 20Pa,

and a time of 8min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 1.39, and a drafting ratio of 1.13.

Comparative Example 5

[0056] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 180°C, a pressure of 20Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 2.22, and a drafting ratio of 1.03; and the pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 255°C, a pressure of 35Pa, and a time of 10min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.37, and the drafting ratio of 1.02.

Comparative Example 6

[0057] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 180°C, a pressure of 20Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 2.22, and a drafting ratio of 1.03. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 240°C, a pressure of 30Pa, and a time of 10min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.25, and the drafting ratio of 1.02. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 250°C, a pressure of 30Pa, and a time of 30min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 0.40, and a drafting ratio of 1.00.

Comparative Example 7

[0058] Comparative Example 1 was repeated, except that the pre-oxidizing in the medium temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 253°C, a pressure of 25Pa, and a time of 7min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.41, and the drafting ratio of 1.03. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 265°C, a pressure of 35Pa, and a time of 5min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 2.64, and a drafting ratio of 1.00.

Comparative Example 8

[0059] Comparative Example 1 was repeated, except that the pre-oxidizing in the medium temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 240°C, a pressure of 78Pa, and a time of 15min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 2.17, and the drafting ratio of 1.03. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 265°C, a pressure of 35Pa, and a time of 5min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 2.64, and a drafting ratio of 1.00.

Comparative Example 9

[0060] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 217°C, a pressure of 150Pa, and a time of 8min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 8.64, and a drafting ratio of 1.07. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 255°C, a pressure of 110Pa, and a time of 30min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.43, and the drafting ratio of 1.02. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 262°C, a pressure of 35Pa, and a time of 30min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 0.44, and a drafting ratio of 1.00.

Comparative Example 10

[0061] Comparative Example 9 was repeated, except that the pre-oxidizing in the high temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: temperature of 265°C, pressure of 160 Pa,

time of 12 min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 5.03, and a drafting ratio of 1.00.

Comparative Example 11

[0062] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 185°C, a pressure of 16Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 1.59, and a drafting ratio of 1.00. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 235°C, a pressure of 30Pa, and a time of 8min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.43, and the drafting ratio of 1.03. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 265°C, a pressure of 105Pa, and a time of 18min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 2.20, and a drafting ratio of 1.00.

Comparative Example 12

[0063] Comparative Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 195°C, a pressure of 18Pa, and a time of 6min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 1.53, and a drafting ratio of 1.03. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 238°C, a pressure of 27Pa, and a time of 8min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.42, and the drafting ratio of 1.03. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 260°C, a pressure of 125Pa, and a time of 20min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 2.40, and a drafting ratio of 1.00.

Example 1

[0064] The polyacrylonitrile-based precursor fiber was subjected to pre-oxidizing in a low temperature section, under conditions of: a temperature of 200°C, a pressure of 20Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 3.33, and a drafting ratio of 1.06; then pre-oxidizing in a medium temperature section, under conditions of: a temperature of 240°C, a pressure of 30Pa, and a time of 20min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.625, and a drafting ratio of 1.03; finally, pre-oxidizing in a high temperature section, under conditions of: a temperature of 250°C, a pressure of 40Pa, and a time of 15min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 1.06, and a drafting ratio of 1.00, to obtain a polyacrylonitrile-based pre-oxidized fiber.

[0065] The polyacrylonitrile-based pre-oxidized fiber was subjected to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence under high-purity nitrogen, to obtain a polyacrylonitrile-based carbon fiber. The carbonizing at the low temperature was operated in four temperature zones having temperatures of 320°C-400°C-550°C-700°C, for a total time of 3 min, at a drafting ratio of 1.06; the carbonizing at the high temperature was operated in four temperature zones having temperatures of 1100°C-1200°C-1300°C-1450°C, for a total time of 2 min, at a drafting ratio of 0.96; the graphitizing was operated at a temperature of 2500°C and a drafting ratio of 1.04 for a time of 3 min.

[0066] The polyacrylonitrile-based pre-oxidized fiber and the polyacrylonitrile-based carbon fiber were subjected to testing and calculating of parameters as mentioned above. The results were shown in Table 1.

Example 2

[0067] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 35Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 5.83, and a drafting ratio of 1.03.

Example 3

[0068] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-

based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 50Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 8.33, and a drafting ratio of 1.05.

Example 4

[0069] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 35Pa, and a time of 4min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 4.17, and a drafting ratio of 1.05.

Example 5

[0070] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 50Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 4.76, and a drafting ratio of 1.05.

Example 6

[0071] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 20Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 3.33, and a drafting ratio of 1.05. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 245°C, a pressure of 30Pa, and a time of 20min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.61, and a drafting ratio of 1.02.

Example 7

[0072] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 20Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 3.33, and a drafting ratio of 1.02. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 245°C, a pressure of 50Pa, and a time of 20min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.02, and a drafting ratio of 1.02.

Example 8

[0073] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 50Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 4.76, and a drafting ratio of 1.05. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 250°C, a pressure of 60Pa, and a time of 22min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.09, and a drafting ratio of 1.03.

Example 9

[0074] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 50Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 4.76, and a drafting ratio of 1.05. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 250°C, a pressure of 60Pa, and a time of 25min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.96, and a drafting ratio of 1.02.

Example 10

[0075] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 20Pa, and a time of

Example 15

[0080] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 20Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 3.33, and a drafting ratio of 1.08. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 245°C, a pressure of 30Pa, and a time of 20min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.61, and a drafting ratio of 1.05. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 260°C, a pressure of 70Pa, and a time of 18min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 1.58, and a drafting ratio of 1.00.

Example 16

[0081] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 40Pa, and a time of 3min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 6.35, and a drafting ratio of 1.05. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 245°C, a pressure of 50Pa, and a time of 22min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.93, and a drafting ratio of 1.02. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 258°C, a pressure of 75Pa, and a time of 15min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 1.94, and a drafting ratio of 1.00.

Example 17

[0082] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 40Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 3.81, and a drafting ratio of 1.07. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 245°C, a pressure of 60Pa, and a time of 22min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.11, and a drafting ratio of 1.05. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 258°C, a pressure of 75Pa, and a time of 17min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 1.71, and a drafting ratio of 1.00.

Example 18

[0083] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 210°C, a pressure of 50Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 4.76, and a drafting ratio of 1.10. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 248°C, a pressure of 60Pa, and a time of 25min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 0.97, and a drafting ratio of 1.05. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 258°C, a pressure of 80Pa, and a time of 17min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 1.82, and a drafting ratio of 1.00.

Example 19

[0084] Example 1 was repeated, except that the pre-oxidizing in the low temperature section of the polyacrylonitrile-based precursor fiber was operated under conditions of: a temperature of 200°C, a pressure of 50Pa, and a time of 5min, which indicated that the pre-oxidizing in the low temperature section had a processing parameter C1 of 5.00, and a drafting ratio of 1.10. The pre-oxidizing in the medium temperature section was operated under conditions of: a temperature of 250°C, a pressure of 60Pa, and a time of 20min, which indicated that the pre-oxidizing in the medium temperature section had a processing parameter C2 of 1.20, and a drafting ratio of 1.05. The pre-oxidizing in the high temperature section was operated under conditions of: a temperature of 260°C, a pressure of 80Pa, and a time of 15min, which indicated that the pre-oxidizing in the high temperature section had a processing parameter C3 of 2.05,

and a drafting ratio of 1.00.

Table 1. results of the testing and calculating of parameters in Comparative Examples and Examples

No.	polyacrylonitrile-based pre-oxidized fiber					polyacrylonitrile-based carbon fiber	
	η (%)	T (cN)	d (μm)	ΔO (wt%)	Characteristic tensile parameter	tensile strength (MPa)	tensile modulus (GPa)
CE.1	47.7	1.96	6.8	3.13	605.52	3821	522
CE.2	48.0	1.93	6.5	3.44	617.36	3744	528
CE.3	48.5	1.81	6.3	3.68	593.12	3723	521
CE.4	63.2	2.15	5.8	2.97	586.58	3855	527
CE.5	50.1	2.41	10.8	4.17	446.01	3912	530
CE.6	49.0	2.22	11.0	3.25	412.69	3826	535
CE.7	76.0	1.83	6.7	3.45	359.39	3919	531
CE.8	72.3	2.15	6.7	3.01	443.84	3853	529
CE.9	81.1	2.41	7.3	3.08	407.07	3814	536
CE.10	85.6	1.76	7.3	4.75	281.65	3723	538
CE.11	61.3	5.38	11.7	3.56	750.13	3512	522
CE.12	63.5	5.50	11.7	3.77	740.29	3569	527
Ex.1	74.0	2.50	7.1	2.78	482.62	4434	540
Ex.2	74.2	2.60	7.1	2.85	493.33	4428	540
Ex.3	74.4	2.68	7.2	2.82	501.11	4401	540
Ex.4	76.6	2.80	7.2	2.58	507.22	4489	541
Ex.5	74.0	2.71	7.2	2.65	508.11	4386	544
Ex.6	75.5	2.92	7.5	2.63	515.36	4415	545
Ex.7	78.1	3.12	7.7	2.34	519.62	4822	546
Ex.8	75.2	2.90	7.4	2.28	522.00	4885	549
Ex.9	77.1	3.02	7.5	2.25	522.97	4921	549
Ex.10	74.2	3.06	7.8	1.98	528.65	4752	549
Ex.11	75.9	3.35	8.2	1.95	538.62	5002	550
Ex.12	75.4	3.47	8.5	1.98	542.11	5012	551
Ex.13	78.2	3.69	8.7	1.85	542.98	5083	550
Ex.14	77.1	3.68	8.7	1.93	548.63	5034	550
Ex.15	80.2	4.06	9.1	1.85	556.69	4902	550
Ex.16	85.2	4.53	9.4	1.94	566.36	4985	550
Ex.17	87.1	4.51	9.1	1.92	569.02	4873	551
Ex.18	89.3	5.08	10.0	1.88	568.87	4637	548
Ex.19	91.0	5.20	10.0	1.83	571.43	4733	549

[0085] As could be seen from the above results, the polyacrylonitrile-based pre-oxidized fiber in accordance with the present disclosure had a characteristic tensile parameter in a specific range, and the carbon fiber prepared from the same had improved mechanical properties.

[0086] The detailed description describes the preferred embodiments of the present disclosure. However, the present disclosure is not limited to the special details of the above embodiments. Various simple modifications may be made to the solutions of the present disclosure within the technical scope of the present invention. Those simple

modifications should also be regarded as being within the protection scope of the present disclosure.

[0087] Further, it should be noted that the specific technical features described in the above embodiments can be combined in any suitable way without contradiction. To avoid unnecessary repetition, various possible combinations are not separately described.

[0088] In addition, any combinations of various embodiments of the present disclosure may be made as long as they are not away from the concept of the present disclosure. Those combinations should also be regarded as the contents of the present disclosure.

Claims

1. A polyacrylonitrile-based pre-oxidized fiber, comprising a core and a shell wrapping the core, wherein the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter A of 475.0-580.0 cN/ μ m, wherein the characteristic tensile parameter A is represented as formula (1):

$$A = \frac{1000 \times T}{\eta \cdot d}; \quad (1)$$

wherein, in formula (1), A represents the characteristic tensile parameter of the polyacrylonitrile-based pre-oxidized fiber (cN/ μ m), T represents fracture strength of the polyacrylonitrile-based pre-oxidized fiber (cN), η represents a ratio of the radial cross-section area of the shell to the radial cross-section area of the entire polyacrylonitrile-based pre-oxidized fiber, and d represents a diameter of the polyacrylonitrile-based pre-oxidized fiber (μ m).

2. The polyacrylonitrile-based pre-oxidized fiber of claim 1, **characterized in that**, in the formula (1),

1.5 cN $\leq$ T $\leq$ 8.0 cN, preferably, 2.5 cN $\leq$ T $\leq$ 5.2 cN; and/or
55% $\leq \eta \leq$ 95%, preferably, 74% $\leq \eta \leq$ 91%; and/or
5.0 μ m $\leq d \leq$ 15.0 μ m, preferably, 7.0 μ m $\leq d \leq$ 10.0 μ m.

3. The polyacrylonitrile-based pre-oxidized fiber of claim 1 or 2, **characterized in that**, the polyacrylonitrile-based pre-oxidized fiber has a characteristic tensile parameter of 480.0-575.0 cN/ μ m, preferably 482.5-571.5 cN/ μ m.

4. The polyacrylonitrile-based pre-oxidized fiber of claim 1, **characterized in that**, the oxygen content difference between the outer area and the inner area of the shell of the polyacrylonitrile-based pre-oxidized fiber is 1.5wt%-3.2wt%, preferably 1.8wt%-2.9wt%; preferably, the outer area of the shell of the pre-oxidized fiber has an oxygen content of 9.0wt%-14.0wt%, preferably 10.5wt%-12.0wt%; the inner area of the shell of the pre-oxidized fiber has an oxygen content of 9.0wt%-11.5wt%, preferably 9.5wt%-10.2wt%.

5. A polyacrylonitrile-based carbon fiber, which is prepared from the polyacrylonitrile-based pre-oxidized fiber of claim 1, and has a tensile strength of greater than or equal to 4000 MPa, preferably greater than or equal to 5000 MPa, and a tensile modulus of 500-600 GPa, preferably 540-570 GPa.

6. A method for preparing a polyacrylonitrile-based pre-oxidized fiber, preferably for preparing the polyacrylonitrile-based pre-oxidized fiber of claim 1, comprising steps of: subjecting a polyacrylonitrile-based precursor fiber to pre-oxidizing in a low temperature section, pre-oxidizing in a medium temperature section and pre-oxidizing in a high temperature section in sequence, to obtain the polyacrylonitrile-based pre-oxidized fiber;

wherein the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section are controlled to have a processing parameter, $C_i =$

$$\frac{100P_i}{T_i t_i}, \text{ satisfying formula (2):}$$

$$N_{i, \min} \leq \frac{100P_i}{T_i t_i} \leq N_{i, \max}; \quad (2)$$

wherein, i = 1, 2, 3, corresponding to the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section respectively; P_i is the

pressure for each pre-oxidizing (Pa); T_1 is the temperature for each pre-oxidizing ($^{\circ}\text{C}$); t_1 is the time for each pre-oxidizing (min),

wherein, for the pre-oxidizing in the low temperature section, $1.00 \leq C_1 \leq 10.00$, preferably $1.90 \leq C_1 \leq 8.33$; for the pre-oxidizing in the medium temperature section, $0.10 \leq C_2 \leq 2.50$, preferably $0.48 \leq C_2 \leq 1.25$; and, for the pre-oxidizing in the high temperature section, $0.50 \leq C_3 \leq 4.00$, preferably $0.85 \leq C_3 \leq 2.13$

7. The method of claim 6, **characterized in that**,

the pre-oxidizing in the low temperature section is operated under conditions of: a temperature T_1 of $200-210^{\circ}\text{C}$; a time t_1 of no more than 10min, preferably 3-5min; a pressure P_1 of 18-55Pa, preferably 20-50Pa; and/or

the pre-oxidizing in the medium temperature section is operated under conditions of: a temperature T_2 of $240-250^{\circ}\text{C}$, a time t_2 of 20-35min, preferably 20-25min; a pressure P_2 of 25-65Pa, preferably 30-60Pa; and/or

the pre-oxidizing in the high temperature section is operated under conditions of: a temperature T_3 of $245-280^{\circ}\text{C}$, a time t_3 of 15-25min, preferably 15-18min; a pressure P_3 of 35-85Pa, preferably 40-80Pa

8. The method of claim 7, **characterized in that**,

$T_2 = (1.20-1.22) \cdot T_1$, preferably $20^{\circ}\text{C} \leq T_2 - T_1 \leq 50^{\circ}\text{C}$, more preferably $30^{\circ}\text{C} \leq T_2 - T_1 \leq 40^{\circ}\text{C}$; and/or $0^{\circ}\text{C} \leq T_3 - T_2 \leq 20^{\circ}\text{C}$, preferably $5^{\circ}\text{C} \leq T_3 - T_2 \leq 15^{\circ}\text{C}$, more preferably $10^{\circ}\text{C} \leq T_3 - T_2 \leq 15^{\circ}\text{C}$.

9. The method of any one of claims 6-8, **characterized in that**, during the pre-oxidizing in the low temperature section, the pre-oxidizing in the medium temperature section and the pre-oxidizing in the high temperature section, the polyacrylonitrile-based precursor fiber independently has a drafting ratio of 0.80-1.20, preferably 0.90-1.10.

10. A polyacrylonitrile-based pre-oxidized fiber prepared by the method of any one of claims 6-9.

11. A method for preparing a polyacrylonitrile-based carbon fiber, **characterized in that** the method comprises steps of: subjecting a polyacrylonitrile-based pre-oxidized fiber to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence, to obtain the polyacrylonitrile-based carbon fiber, wherein the polyacrylonitrile-based pre-oxidized fiber is the polyacrylonitrile-based pre-oxidized fiber of claim 1 or the polyacrylonitrile-based pre-oxidized fiber prepared by the method of claim 6.

12. The method of claim 11, **characterized in that**,

the carbonizing at the low temperature is operated under conditions of: a temperature of $400-1000^{\circ}\text{C}$, a time of 0.5-10min, and a drafting ratio of 0.80-1.20; and/or

the carbonizing at the high temperature is operated under conditions of: a temperature of $800-1800^{\circ}\text{C}$, a time of 0.5-10min, and a drafting ratio of 0.80-1.00; and/or

the graphitizing is operated under conditions of: a temperature of $2200-3000^{\circ}\text{C}$, a time of 0.2-15min, and a drafting ratio of 0.90-1.50.

13. Use of the polyacrylonitrile-based pre-oxidized fiber of any one of claims 1-4 in preparing a polyacrylonitrile-based carbon fiber, comprising steps of: subjecting the polyacrylonitrile-based pre-oxidized fiber to carbonizing at a low temperature, carbonizing at a high temperature and graphitizing in sequence, to obtain the polyacrylonitrile-based carbon fiber.

14. The use of claim 13, **characterized in that**,

the carbonizing at the low temperature is operated under conditions of: a temperature of $400-1000^{\circ}\text{C}$, a time of 0.5-10min, and a drafting ratio of 0.80-1.20; and/or

the carbonizing at the high temperature is operated under conditions of: a temperature of $800-1800^{\circ}\text{C}$, a time of 0.5-10min, and a drafting ratio of 0.80-1.02; and/or

the graphitizing is operated under conditions of: a temperature of $2200-3000^{\circ}\text{C}$, a time of 0.2-15min, and a drafting ratio of 0.90-1.50.



Fig. 1

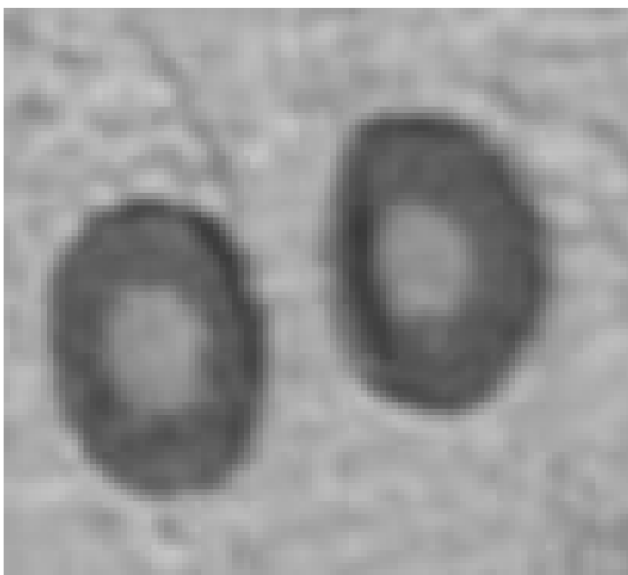


Fig. 2

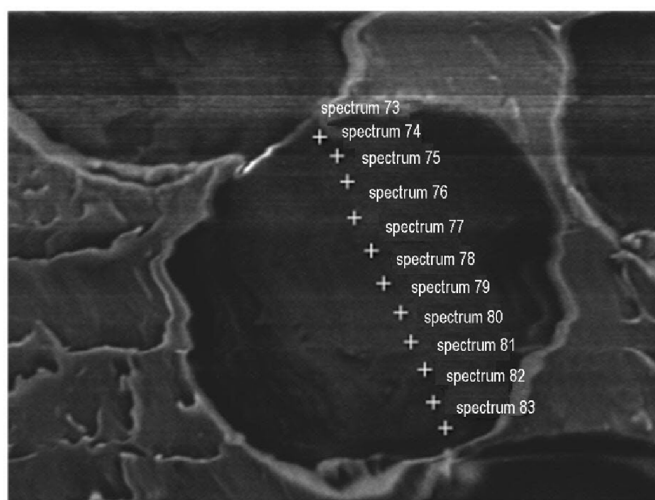


Fig. 3

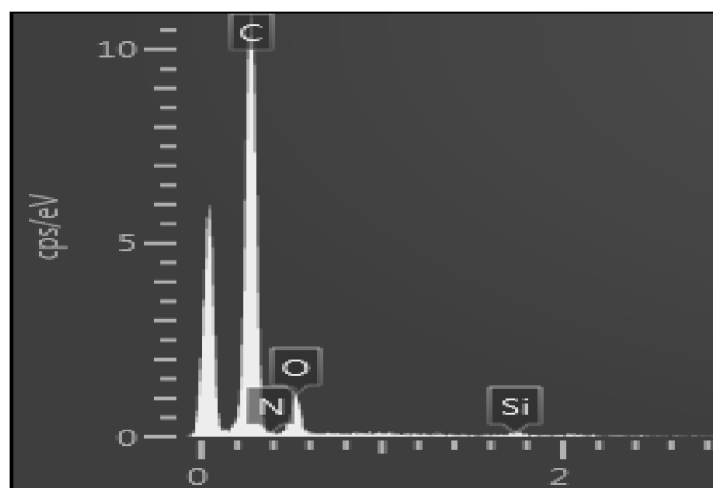


Fig. 4

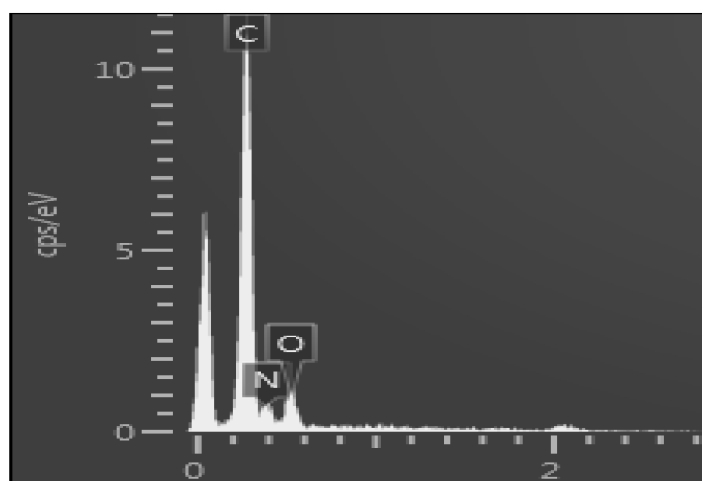


Fig. 5

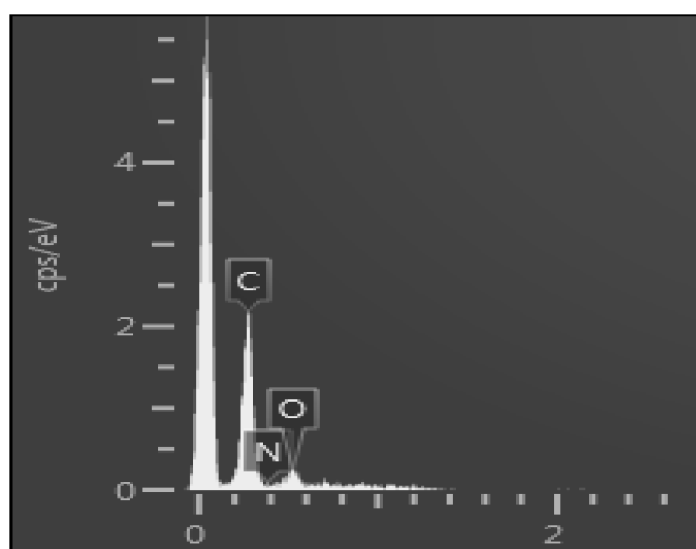


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2024/122201

A. CLASSIFICATION OF SUBJECT MATTER

D01F9/22(2006.01)i

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)

IPC: D01F9

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT, ENTXTC, VEN, CJFD, CNKI, ISI Web of Science: 聚丙烯腈, 预氧丝, 皮, 芯, 断裂强力, 温度, 压力, 时间, 碳化, 石墨化, polyacrylonitrile, PAN, pre-oxidation, fiber, skin, core, breaking strength, temperature, pressure, carbonization, graphitization

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 110067044 A (SHANXI INSTITUTE OF COAL CHEMISTRY, CHINESE ACADEMY OF SCIENCES) 30 July 2019 (2019-07-30) description, paragraphs 0007-0020	5
X	CN 114059197 A (KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY) 18 February 2022 (2022-02-18) description, embodiments 3-4, and comparative examples 2 and 3	5
A	CN 110067044 A (SHANXI INSTITUTE OF COAL CHEMISTRY, CHINESE ACADEMY OF SCIENCES) 30 July 2019 (2019-07-30) description, paragraphs 0007-0020	1-4, 6-14
A	CN 114059197 A (KUNMING UNIVERSITY OF SCIENCE AND TECHNOLOGY) 18 February 2022 (2022-02-18) description, embodiments 3-4, and comparative examples 2 and 3	1-4, 6-14
A	CN 110106584 A (GLOBAL ENERGY INTERCONNECTION RESEARCH INSTITUTE CO., LTD. et al.) 09 August 2019 (2019-08-09) description, abstract	1-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D" document cited by the applicant in the international application	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E" earlier application or patent but published on or after the international filing date	"&" document member of the same patent family
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 11 December 2024	Date of mailing of the international search report 02 January 2025
Name and mailing address of the ISA/CN China National Intellectual Property Administration (ISA/CN) China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088	Authorized officer Telephone No.

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PCT/CN2024/122201

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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 111691011 A (SHANXI GANGKE CARBON MATERIALS CO., LTD.) 22 September 2020 (2020-09-22) claims 1-9	1-14
A	CN 116876115 A (NINGBO INSTITUTE OF MATERIALS TECHNOLOGY AND ENGINEERING, CHINESE ACADEMY OF SCIENCES) 13 October 2023 (2023-10-13) claims 1-10	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2024/122201

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	110067044	A	30 July 2019	CN	110067044	B	28 July 2020
CN	114059197	A	18 February 2022	None			
CN	110106584	A	09 August 2019	CN	110106584	B	30 November 2021
CN	111691011	A	22 September 2020	CN	111691011	B	29 November 2022
CN	116876115	A	13 October 2023	None			

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- GB/T 14337-2008 [0018] [0047]
- GB/T25749-2011 [0049]