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(54) **Pitch based carbon fibres and process for producing the same.**

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(73) Proprietor: **NIPPON OIL COMPANY, LIMITED**
3-12, 1-chome, Nishi-Shimbashi
Minato-ku
Tokyo (JP)

(72) Inventor: **Uemura, Seiichi**
2-22-18 Higashi-Yukigaya,
Ota-ku
Tokyo (JP)
Inventor: **Kato, Osamu**
609 Niiharu-cho,
Midori-ku
Yokohama-shi,
Kanagawa-ken (JP)
Inventor: **Takashima, Hiroaki**
2-228 Kosugi-cho,
Nakahara-ku
Kawasaki-shi,
Kanagawa-ken (JP)

(74) Representative: **Cropp, John Anthony David et**
al
MATHYS & SOUIRE
100 Grays Inn Road
London, WC1X 8AL (GB)

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EP 0 384 761 B1

Description

Background of the Invention

The present invention relates to a carbon fiber having a novel structure.

It is known that a carbon fiber having high strength and high elastic modulus can be produced by heat-treating pitch to form mesophase, then melt-spinning the resulting mesophase pitch and subjecting the resulting pitch fiber to infusibilizing, carbonizing and graphitizing treatments (USP4005183). The carbon fiber thereby obtained has a tensile strength of about 981 to 1962 N/mm² (100 to 200 kg/mm²) and an elastic modulus of about 156200 to 686700 N/mm² (20 to 70 ton/mm²). An alternative process for producing carbon fibers is described in US4208267.

If the carbonized fiber obtained using mesophase pitch is calcined in a graphitization region of 2,500° to 3,000°C, a graphitized structure develops and the elastic modulus increases as the calcining temperature rises. More particularly, it has been reported that an inter layer spacing (d_{002}), which can be said to be a measure of graphitization, becomes narrower with an increase of the calcining temperature and that the value or d_{002} is 3.37Å or smaller when the carbonized fiber is calcined in the graphitization region (USP4005183).

Further, the pitch based carbon fiber thus obtained has a three-dimensional order of a polycrystalline graphite which is characterized by the presence of cross lattice line (112) and lines (100) and (101) in an X-ray diffraction pattern thereof.

On the other hand, with development of the graphitized structure, there occurs shrinkage of the carbon layer surface and cracking of the fiber along the fiber axis. This cracking causes deterioration in mechanical strength of the fiber. The carbonized fiber obtained from mesophase pitch is constituted by a giant domain (a carbon layer having a hexagonal net structure) extending straight in the fiber axis direction, so when graphitized, it easily causes cracks. Therefore, when pitch is used as a starting material, it is difficult to obtain a carbon fiber high in strength (e.g. 250 kg/mm² or more) although there is obtained a carbon fiber having a high elastic modulus.

Summary of the Invention

It is the object of the present invention to provide a carbon fiber having such a high strength as has been unattained by conventional pitch based carbon fibers.

Having made extensive studies for achieving the above object, the present inventors developed

a carbon fiber having a novel structure which is entirely different from the structure of conventional pitch based carbon fibers. The carbon fiber of the present invention possesses a remarkably improved mechanical strength based on its unique structure.

More specifically, the present invention resides in a pitch based carbon fiber having (100) and (101) lines and not having (112) line in an X-ray diffraction pattern thereof, having an interlayer spacing d_{002} of 3.38 to 3.43Å, and further having a corrugated carbon layer, with pitches of the corrugation being in the range of 300 to 3,000Å.

In a second aspect of the present invention there is provided a process for producing the above pitch based carbon fiber, which combine melt-spinning an optically anisotropic pitch at a melt-spinning viscosity in the range of 300 to 3,000 poise, using a melt-spinning apparatus provided with a nozzle having an elongate member disposed therein to form a space between the inner wall of said nozzle and said elongate member disposed in the nozzle, the area in any cross-section of said space being larger than the sectional area of a downstream capillary portion of the nozzle; then subjecting the resulting pitch fiber to an infusibilization treatment and subsequently to a carbonization treatment.

A nozzle of the aforementioned type is described in detail in US4717331.

Detailed Description of the Invention

Regarding the crystallite size, as determined by X-ray diffraction, of the carbon fiber of the present invention, L_c is in the range of 100 to 300Å, preferably 150 to 200Å, and L_a is in the range of 50 to 200Å, preferably 70 to 160Å. The interlayer spacing d_{002} is in the range of 3.38 to 3.43Å, preferably 3.39 to 3.42Å. Even when calcined in the graphitization region of 2,500° to 3,000°C, d_{002} is not smaller than 3.38Å and does not become 3.37Å or smaller. This is an outstanding feature.

The carbon fiber of the present invention, in an X-ray diffraction pattern thereof, possesses (100) and (101) lines, but does not possess (112) line. This is also a characteristic feature of the carbon fiber of the present invention.

The above points are based on a novel structure of the carbon fiber of the present invention which is different from the conventional structure. More specifically, the pitch based carbon fiber of the present invention has a corrugated domain of a carbon layer having a hexagonal net structure. Therefore, even when it is calcined at a temperature of 2,500° to 3,000°C, there is little shrinkage of the carbon layer surface and the interlayer spac-

ing does not become 3.37Å or smaller. For this reason, cracking of the fiber does not occur. Further, since the domain is corrugated, even if a part of the domain is cracked, the cracking will be terminated by the convex portion of the corrugation closest to the crack, thereby preventing the cracking from spreading all over the domain. As a result, a high strength is maintained. On the other hand, the domain in conventional carbon fibers is in the form of a flat plate, so once cracking occurs at one end thereof, it extends to the other end immediately, resulting in cracking all over the domain, and hence the strength deteriorates rapidly.

When the carbon fiber of the present invention is observed for its section in the direction perpendicular to the fiber axis using a scanning electron microscope, it can be confirmed that a corrugated carbon layer face is present. The pitch of the corrugation is in the range of 300 to 3,000Å preferably 500 to 2,000Å.

The carbon fiber of the present invention is produced using an optically anisotropic pitch. As the starting material there may be used any of the heavy oils obtained from petroleum or coal. Particularly preferred are petroleum-based heavy oils boiling not lower than 200°C, especially not lower than 300°C, which are obtained in fluid catalytic cracking of petroleums, e.g. vacuum gas oil.

It is desirable that insoluble solids such as the residue of catalyst contained in a heavy oil to be used be separated and removed prior to the spinning pitch producing step, preferably to the extent of not higher than 50 ppm, more preferably not higher than 30ppm, in terms of an insoluble solids content. How to separate and remove such insoluble solids is not specially limited. For example, there may be adopted filtration using a filter or centrifugal separation prior to filtration, the heavy oil may be subjected to a hydrogenation treatment or a heat treatment.

The heavy oil after the separation and removal of insoluble solids is heat-treated usually at a temperature of 340° to 450°C for 1 to 50 hours, at atmospheric pressure or reduced pressure while passing or without passing an inert gas such as nitrogen gas or steam, to obtain a spinning pitch containing an optically anisotropic phase (e.g. 60-100 vol%). Prior to the spinning pitch producing step, the heavy oil after the separation and removal of insoluble solids is preferably subjected to a preliminary heat treatment to distill off light fractions, whereby the time required for producing the spinning pitch is shortened.

The spinning pitch is then melt-spun usually at a temperature higher by 30° to 80° than the softening point thereof. For the melt spinning there is used a melt spinning apparatus having a nozzle within which is disposed an elongate member, e.g.

a molded member to form a space serving as a melt flow path, generally an annular melt flow path, between the elongate member and the inner wall of the nozzle. The elongate member as referred to herein indicates a molded product whose height is longer than the width thereof. Its shape is not limited. For example, it may be in the shape of a cylinder, a semi-cylinder, a circular cone, a prism, a pyramid, an ellipsoid, a plate, or a suitable combined shape thereof. Preferably, these shapes each have a slot or a projection on the side face thereof. As the slot, a spiral slot such as drill- or screw-like slot is particularly preferred.

It is necessary that in any cross section of the elongate member disposed in the nozzle there is formed a space serving as a melt flow path between the inner wall of the nozzle and the said elongate member, and that the area of the said space is larger than the sectional area of a capillary portion (orifice channel) of the nozzle. An example of the nozzle and elongate member arrangement is shown in Figure 3.

The spinning is performed at a temperature in the range of 280° to 360°C, preferably 300° to 340°C. Under spinning conditions, the viscosity of the pitch used is in the range of 30 to 300 Pas (300 to 3,000 poise), preferably 50 to 200 Pas (500 to 2,000 poise), more preferably 70 to 150 Pas (700 to 1,500 poise).

The pitch fiber obtained by the melt spinning is wound round a bobbin or accumulated in a container or the like preferably while applying a sizing agent thereto.

The pitch fiber is then rendered infusible. In this case the pitch fiber which has been wound round a bobbin is held in that state or in an accumulated state in a container or the like after being delivered from the bobbin, or the pitch fiber which has been accumulated in a container or the like from the beginning is held in the accumulated state.

The infusibilizing treatment is conducted in an oxidizing gas atmosphere at a temperature of 150° to 380°C, preferably 180° to 350°C, usually for 5 minutes to 3 hours, preferably 10 minutes to 2 hours.

As the oxidizing gas there may be used one or more substances (e.g. air containing 0.1 to 30 vol% of NO₂), mixtures of air, oxygen, ozone, nitrogen oxide, halogen and sulfurous acid gas.

The fiber thus rendered infusible is then subjected to a carbonization treatment (including graphitization) at 1,200° to 3,000°C in an inert gas atmosphere such as nitrogen gas or argon. Prior to this carbonization treatment the fiber may be subjected to a preliminary carbonization treatment in an inert gas atmosphere at a temperature up to 850°C, for example, in the range of 500° to

850 °C.

[Example]

The following working example is given to illustrate the present invention

Example 1

A spinning pitch having an optically anisotropic phase content of 95 vol% was melt-spun at a temperature of 320 °C, at a spinning viscosity of 1,000 poise, using a melt spinning apparatus provided with a nozzle having a long, drill-like molded member disposed therein, to afford a pitch fiber.

The pitch fiber was then subjected to an infusibilization treatment at 240 °C for 1 hour in an air atmosphere containing 5 vol% of NO₂. The fiber thus rendered infusible was calcined at 700 °C for 1 hour in an inert gas atmosphere and then carbonized at 2,250 °C to obtain a carbon fiber. The carbon fiber was found to have a tensile strength of 4218 N/mm² (430 kg/mm²) and an elastic modulus in tension of 637650 N/mm² (65 ton/mm²).

Fig. 1 shows a sectional structure of this carbon fiber, from which it is seen that each domain is corrugated. An average pitch of the corrugation was about 700 Å. In an X-ray diffraction pattern of the carbon fiber there were (100) and (101) lines, but (112) line was not present, and the interlayer spacing d_{002} was 3.41 Å.

Thus, the pitch based carbon fiber of the present invention has a novel structure, and this structure permits the carbon fiber to have a high elastic modulus and a remarkably high mechanical strength, for example, a tensile strength of 3924 N/mm² (400 kg/mm²) or higher.

Brief Description of the Figures

Fig. 1 is a photograph taken by an electron microscope, showing a sectional structure of the carbon fiber of the present invention, and Fig. 2 is an enlargement thereof.

Fig. 3 is a sectional view of the nozzle and elongate member arrangement in a die plate 6 for melt spinning a pitch fibre. The nozzle has a capillary channel 5, a counterbore orifice 7 of greater cross sectional dimension than that of the capillary channel, said orifice defining a cavity, an elongate member 10 centrally disposed within the cavity by a fixing plate 9, at a predetermined spacing between said elongate member and the inner surface of the cavity, said spacing defining an annular pitch flow path communicating with capillary channel 5.

For better particulars of a suitable combination of nozzle and elongate member reference should be made to USP 4,717,331.

Claims

1. A pitch based carbon fiber having in an X-ray diffraction pattern thereof (100) and (101) lines and not having (112) line, characterised in that the pitch based carbon fiber has an interlayer spacing in the range of from 3.38 to 3.43 Å, and further having a corrugated carbon layer, with pitches of the corrugation being in the range of 300 to 3,000 Å.
2. A process for producing the pitch based carbon fiber of Claim 1, which process comprises melt-spinning an optically anisotropic pitch at a melt-spinning viscosity in the range of 30 to 300 Pas (300 to 3,000 poise,) using a melt-spinning apparatus provided with a nozzle having an elongate member (10) disposed therein to form a space between the inner wall of said nozzle and said elongate member disposed in the nozzle, the area in any cross-section of said space being larger than the sectional area of a downstream capillary portion (5) of the nozzle; then subjecting the resulting pitch fiber to an infusibilization treatment and subsequently to a carbonization treatment.
3. A process as set forth in Claim 1 or 2, wherein said pitch has an optically anisotropic phase content in the range of 60 to 100% by volume.
4. A process as set forth in Claim 2, wherein said long molded member has a side face formed with a spiral slot.
5. A process as set forth in Claim 2 or 4, wherein the melt-spinning viscosity is in the range of 50 to 200 Pas (500 to 2,000 poise)
6. A process as set forth in Claim 2, 4 or 5 wherein the spinning temperature is in the range of 280 ° to 360 °C.
7. A process as set forth in Claim 2 or any one of Claims 4 to 6, wherein said infusibilization treatment is performed in an oxidizing gas atmosphere at a temperature of 150 ° to 380 °C for 5 minutes.
8. A process as set forth in Claim 2 or any one of Claims 4 to 7, wherein said carbonization treatment is performed in an inert gas atmosphere at a temperature of 1,200 ° to 3,000 °C.

Patentansprüche

1. Kohlenstoffaser auf Pechbasis, welche ein Röntgenbeugungsmuster mit (100)- und (101)-

aber ohne (112)-Linien aufweist, dadurch gekennzeichnet, daß die Kohlenstoffaser auf Pechbasis einen Abstand zwischen den einzelnen Lagen im Bereich von 3,38 bis 3,43 Å und darüber hinaus eine geriefte Kohlenstoffschicht aufweist, wobei der Abstand der Riefen im Bereich von 300 bis 3000 Å liegt.

2. Verfahren zur Herstellung einer Kohlenstoffaser auf Pechbasis gemäß Anspruch 1, welches das Schmelzspinnen eines optisch anisotropen Pechs bei einer Schmelzspinnviskosität im Bereich von 30 bis 300 Pa·s (300 bis 3000 Poise) unter Verwendung einer Schmelzspinnvorrichtung, die mit einer Düse versehen ist, in der ein längliches Bauteil (10) angeordnet ist, welches so ausgebildet ist, daß zwischen der inneren Wandung der Düse und dem in der Düse angebrachten Bauteil ein Raum entsteht, wobei die Fläche jedes Querschnittes dieses Raumes größer als die Querschnittsfläche eines folgenden kapillaren Teils (5) der Düse ist, und das anschließende Unterwerfen der erhaltenen Pechfaser unter eine Behandlung zum Unschmelzbarmachen und danach unter eine Carbonisierungsbehandlung umfaßt. 10 15 20 25
3. Verfahren gemäß Anspruch 1 oder 2, in dem das Pech einen Gehalt an optisch anisotroper Phase von 60 bis 100 Vol.-% aufweist. 30
4. Verfahren gemäß Anspruch 2, bei dem das langgestreckt geformte Bauteil eine mit einer spiralförmigen Nut geformte Seitenfläche aufweist. 35
5. Verfahren gemäß Anspruch 2 oder 4, bei dem die Schmelzspinnviskosität im Bereich von 50 bis 200 Pa·s (500 bis 2000 Poise) liegt. 40
6. Verfahren gemäß Anspruch 2, 4 oder 5, bei dem die Spinn temperatur im Bereich von 280 bis 360 °C liegt. 45
7. Verfahren gemäß Anspruch 2 oder gemäß einem der Ansprüche 4 bis 6, bei dem die Behandlung zum Umschmelzbarmachen 5 Minuten lang in einer oxidierenden Gasatmosphäre bei einer Temperatur von 150 bis 380 °C durchgeführt wird. 50
8. Verfahren gemäß Anspruch 2 oder gemäß einem der Ansprüche 4 bis 7, bei dem die Carbonisierungsbehandlung in einer Inertgasatmosphäre bei einer Temperatur von 1200 bis 3000 °C durchgeführt wird. 55

Revendications

1. Fibre de carbone à base de brai ayant dans un spectre de diffraction des rayons X de celle-ci, des raies (100) et (101) et n'ayant pas de raie (112), caractérisée en ce que la libre de carbone à base de brai a un espacement entre les couches dans la gamme de 3,38 à 3,43Å et a de plus une couche de carbone ondulée, avec des pas de l'ondulation étant compris dans la gamme de 300 à 3.000Å.
2. Procédé pour la production de la fibre de carbone à base de brai suivant la revendication 1, lequel procédé comprend le filage à l'état fondu d'un brai optiquement anisotrope à une viscosité de filage à l'état fond dans la gamme de 30 à 300 Pa.s (300 à 3.000 poises) avec un appareil de filage à l'état fondu équipé d'une buse dans laquelle est disposé un membre allongé (10) de façon à former un espace entre la paroi intérieure de cette buse et cet élément allongé disposé dans la buse, la surface d'une quelconque section droite de cet espace étant supérieure à la surface en section droite d'une portion capillaire (5) en aval de la buse; puis la soumission de la fibre de brai résultante à un traitement d'infusibilisation et ensuite à un traitement de carbonisation.
3. Procédé suivant les revendications 1 ou 2, dans lequel ce brai a une teneur en phase optiquement anisotrope dans la gamme de 60 à 100% en volume.
4. Procédé suivant la revendication 2, dans lequel ce long élément moulé a une face latérale formée avec une fente en spirale.
5. Procédé suivant les revendications 2 ou 4, dans lequel la viscosité de filage à l'état fondu est de 50 à 200 Pa.s (500 à 2.000 poises).
6. Procédé suivant les revendications 2, 4 ou 5, dans lequel la température de filage est dans la gamme de 280 °C à 360 °C.
7. Procédé suivant la revendication 2 ou l'une quelconque des revendications 4 à 6, dans lequel ce traitement d'infusibilisation est conduit dans une atmosphère de gaz oxydant à une température de 150 °C à 380 °C pendant 5 minutes.
8. Procédé suivant la revendication 2 ou l'une quelconque des revendications 4 à 7, dans lequel ce traitement de carbonisation est conduit dans une atmosphère de gaz inerte à

une température de 1.200 °C à 3.000 °C.

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Figure 1

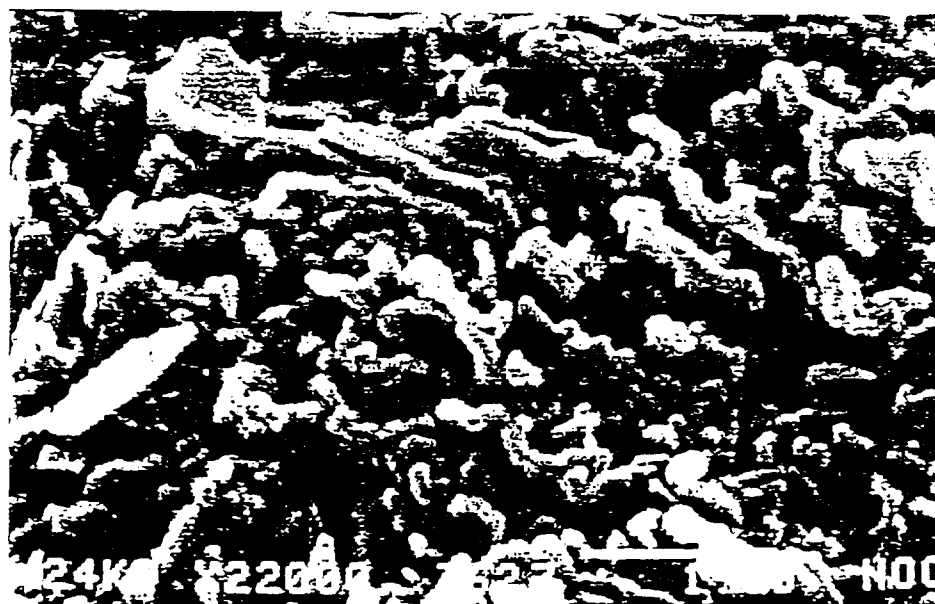


Figure 2

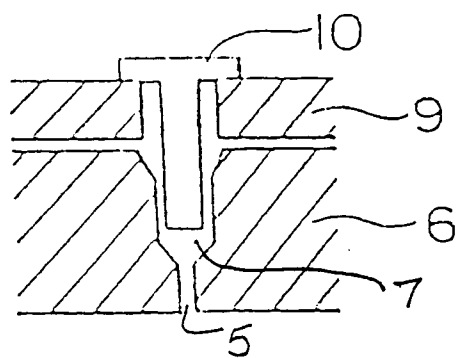


Figure 3