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(54) Pitch based carbon fibers.

(57) A pitch based carbon fiber having a novel structure and an improved mechanical strength is provided. The carbon fiber has, in an X-ray diffraction pattern thereof, (100) and (101) lines, no (112) line, has an interlayer spacing in the range of 3.38 to 3.43Å, and further has a corrugated carbon layer, with pitches of the corrugation being in the range of 300 to 3,000Å.

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Pitch Based Carbon Fibers

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 infusiblizing, carbonizing and graphitizing treatments (USP4005183). The carbon fiber thereby obtained has a tensile strength of about 100 to 200 kg/mm^2 and an elastic modulus of about 20 to 70 ton/mm^2.

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 interlayer spacing (d_{002}) which can be said to be a measure of graphitization becomes narrower with increase of the calcining temperature and that the value of 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), (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 starting 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 higher in strength (e.g. 250 kg/mm^2 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 of a novel structure 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.

Detailed Description of the Invention

Regarding the crystallite size as determined by X-ray diffraction of the carbon fiber of the present invention, Lc is in the range of 100 to 300Å, preferably 150 to 200A, and La 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 diffractions pattern thereof, possesses (100) and (101) lines, but does not possess (112) line. This is also a characteristic feature thereof.

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 spacing does not become 3.37A 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 is deteriorated 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 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 300 to 3,000 poise, preferably 500 to 2,000 poise, more preferably 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 infusiblizing 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 (e.g. air containing 0.1 to 30 vol% of NO_2) 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 infusiblization treatment at 240°C for 1 hour in an air atmosphere containing 5 vol% of NO_2. 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 430 kg/mm^2 and an elastic modulus in tension of 65 ton/mm^2.

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 700Å. 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 3.41Å.

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 strenth, for example, a tensile strength of 400 kg/mm^2 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 that 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, not having (112) line, also having an interlayer spacing in the range 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.

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 300 to 3,000 poise, using a melt spinning apparatus provided with a nozzle having an elongate member disposed therein, then subjecting the resulting pitch fiber to an infusiblization treatment and subsequently to a carbonization treatment.

3. A process as set forth in Claim 2, wherein said pitch has an optically anisotropic phase content in the range or 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, wherein a space is formed 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 capillary portion of the nozzle.

6. A process as set forth in Claim 2, wherein the melt-spinning viscosity is in the range of 500 to 2,000 poise.

7. A process as set forth in Claim 2, wherein the spinning temperature is in the range of 280 ° to 360 ° C.

8. A process as set forth in Claim 2, wherein said infusiblization treatment is performed in an oxidizing gas atmosphere at a temperature of 150 to 380 ° C for 5 minutes to 3 hours.

9. A process as set forth in Claim 2, wherein said carbonization treatment is performed in an inert gas atmosphere at a temperature of 1,200 ° to 3,000 ° C.

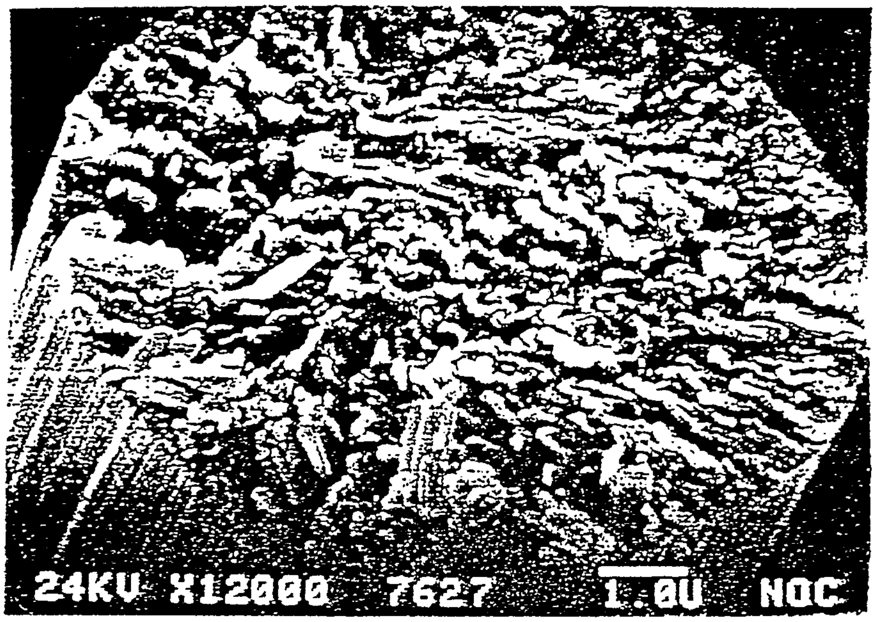

Figure 1

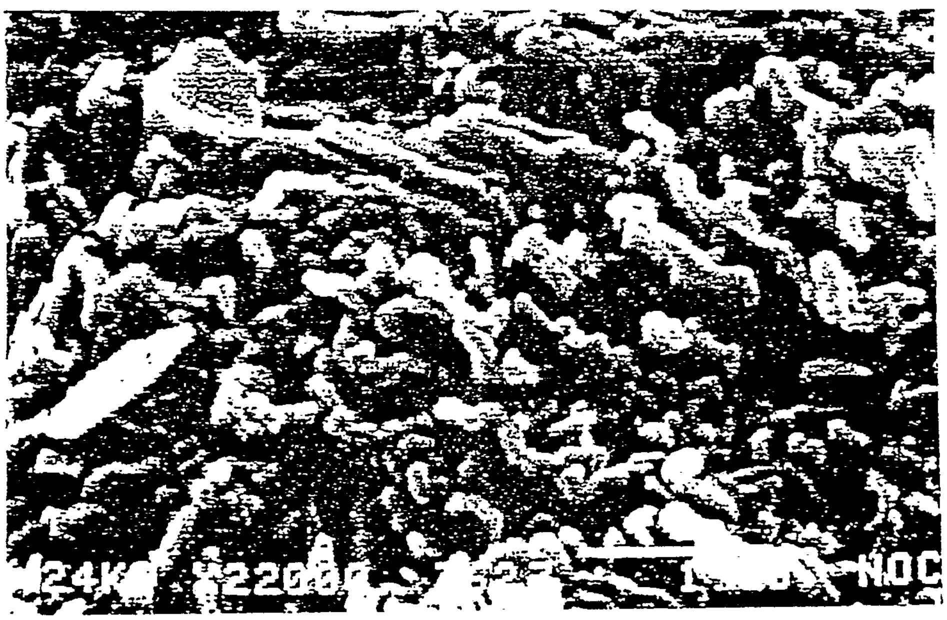

Figure 2

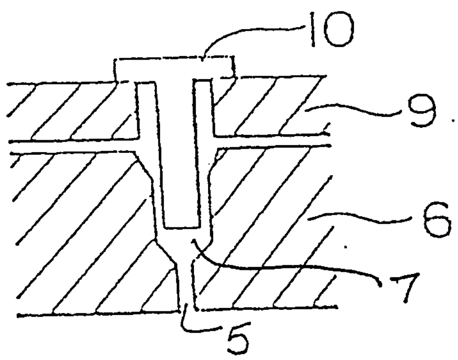

Figure 3