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(54) **Pitch-based carbon fiber.**

(57) A high thermal conductivity pitch-based carbon fiber is characterised by having a thermal conductivity in the axial direction of fiber of 300 to 1500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/density (ρ) of 70 to 500, a degree of agglutination of 0 to 30%, and a compressive strength of 0.2 to 0.5 GPa.

A method of producing high thermal conductivity pitch-based carbon fiber is also disclosed.

EP 0 481 762 A2

BACKGROUND OF THE INVENTION

The present invention generally relates to a carbon fiber. More specifically, the present invention relates to a high thermal conductivity pitch-based carbon fiber having a higher thermal conductivity, a larger compressive strength and excellent yarn handleability and being applicable widely as the carbon fiber reinforced composite materials for printing substrates, IC substrates and heat sinks for electronic devices. The present invention also relates to a method of producing the same.

Description of the Related Art:

A variety of fiber reinforced composite materials have been proposed recently as the materials of printing substrates, IC substrates and heat sinks. High thermal conductivity is particularly indispensable for the fibers to be used in such fiber reinforced composite materials.

PAN-based and pitch-based carbon fibers have conventionally been produced and used widely as the carbon fiber. The mechanical properties of PAN-based carbon fibers are excellent, but the thermal conductivity thereof is distinctively low, generally as low as 10 W/m/K or less. It has not been known any PAN-based carbon fiber with a thermal conductivity of 75 W/m/K or more. There is no expectation of the improvement of the thermal conductivity. PAN-based carbon fibers therefore cannot be used favorably in the carbon fiber reinforced composite materials described hereinabove.

Alternatively, it has not been known any pitch-based carbon fiber with satisfactorily high and balanced mechanical properties, in particular compressive strength and yarn handleability in producing fiber reinforced composite materials.

Enhanced mechanical properties, in particular such as enhanced compressive strength as well as high thermal conductivity, have been demanded for the carbon fiber to be used in the carbon fiber reinforced composite materials for printing substrates and the like mentioned hereinabove.

Carbon fiber may be impregnated with metallic materials in producing thermally conductive members for printing substrates or carbon fiber reinforced composite materials for heat sinks. Particularly in such cases, less fiber agglutination, namely excellent yarn handleability, is required.

During the process of investigating the relation between the thermal conductivity and the mechanical strength with respect to the crystalline structure of a pitch-based carbon fiber, the present inventors have found that an excellent pitch-based carbon fiber of high thermal conductivity can be obtained which is provided with tensile strength and tensile elastic modulus, each above a preset level and has remarkably increased thermal conductivity and compressive strength, by controlling the crystalline structure of the carbon fiber, in particular the stack height (Lc 002), within a specific range, more specifically by controlling the ratio of the stack height (Lc 002)/ the density (ρ) within a specific range, and that the carbon fiber can acquire excellent yarn handleability in producing composite materials to be able to produce superior carbon fiber reinforced composite materials, by the regulation of the degree of agglutination of such carbon fiber at 30% or less.

The present invention has been achieved on such novel findings.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a pitch-based carbon fiber of high thermal conductivity and a method of producing the same, the high thermal conductivity pitch-based carbon fiber having a higher thermal conductivity and a greater compressive strength with no deterioration of tensile strength and tensile elastic modulus, along with excellent yarn handleability.

The object mentioned above can be achieved by a high thermal conductivity pitch-based carbon fiber according to the present invention. The present invention is summarized as a pitch-based carbon fiber of high thermal conductivity, characterized by having a thermal conductivity in the axial direction of fiber of 300 to 1,500 W/m/K, a ratio of stack height (Lc 002)/density (ρ) of 70 to 500, a degree of fiber agglutination of 0 to 30%, and a compressive strength of 0.2 to 0.5 GPa.

The present inventors have found during the process of investigation and development to obtain a pitch-based carbon fiber with excellent thermal conductivity by using pitch as the raw material, that the promotion of crystallization of the fiber is required in order to increase the thermal conductivity in the axial direction of the fiber but the crystallization facilitated too far distinctively reduces the mechanical properties of the fiber, in particular the compressive strength.

The present inventors have thus found that the crystalline structure of a carbon fiber, in particular the stack height (Lc 002) thereof, should be within a specific range; in other words, the ratio of stack height (Lc 002)/-density (ρ) should be in the range of 70 or more to 500 or less, in order to obtain a pitch-based carbon fiber of

high thermal conductivity, having balanced mechanical properties with a thermal conductivity of 300 to 1500 W/m/K and a compressive strength of 0.2 to 0.5 GPa, as well as a tensile strength of 2.5 to 4.5 GPa and a tensile elastic modulus of 700 to 950 GPa. If the ratio of stack height (Lc 002)/density (ρ) is less than 70, the thermal conductivity will not reach 300 W/m/K; if the ratio is above 500 W/m/K, the compressive strength gets smaller than 0.2 GPa, and mechanical properties balanced with tensile strength and tensile elastic modulus cannot be obtained.

More explanation of the high thermal conductivity pitch-based carbon fiber in accordance with the present invention will now follow. In the high thermal conductivity pitch-based carbon fiber in accordance with the present invention, the stack height (Lc 002) is important among the factors defining the crystalline structure. In accordance with the present invention, the stack height (Lc 002) is generally 160 to 1,000 Å while the layer size (La 110) is 200 to 1,000 Å and the interlayer spacing (d_{002}) is 3.36 to 3.40 Å. The dendity (ρ) of the fiber of the present invention is generally 2.16 to 2.24 g/cm^3.

By controlling the degree of agglutination at 30% or less, the yarn handleability of the pitch-based carbon fiber of the present invention in producing a composite material can be improved, whereby an excellent carbon fiber reinforced composite material can be produced. If the degree of agglutination exceeds 30%, the yarn handleability is remarkably reduced; in case that carbon fibers are impregnated with metal such as aluminium to produce a carbon fiber reinforced composite material, for example, each carbon fiber generally comprising 100 to 10,000 filaments is not uniformly impregnated with melted metal, so a carbon fiber reinforced composite material with desirable properties cannot be produced.

Further explanation of the pitch-based carbon fiber in accordance with the present invention will now follow. According to the present invention, there can be obtained a high thermal conductivity pitch-based carbon fiber having a thermal conductivity as high as 300 to 500 W/m/K, and balanced mechanical properties such as a compressive strength of 0.3 to 0.5 GPa, as well as a tensile strength of 2.5 to 4.0 GPa, and a tensile elastic modulus of 700 to 900 GPa; and a high thermal conductivity pitch-type carbon fiber having a thermal conductivity of 500 W/m/K or more, namely 500 to 1500 W/m/K, and balanced mechanical properties such as a compressive strength of 0.2 to 0.4 GPA, as well as a tensile strength of 2.5 to 4.5 GPa, and a tensile elastic modulus of 700 to 950 GPa.

In order to obtain a high thermal conductivity pitch-based carbon fiber having a thermal conductivity as high as 300 to 500 W/m/K, the crystalline structure of the carbon fiber, particularly with respect to stack height (Lc 002), should be within a specific range; more specifically, the ratio of stack height (Lc 002)/density (ρ) should be within the range of 70 or more to 180 or less. In case that the ratio of stack height (Lc 002)/density (ρ) is less than 70, the thermal conductivity will not reach 300 W/m/K; in case that the ratio exceeds 180, the compressive strength gets smaller than 0.3 GPa, and the mechanical properties balanced with tensile strength and tensile elastic modulus cannot be obtained.

For further explanation of the present invention, the stack height (Lc 002) is generally 160 to 400 Å, while the layer size (La 110) is 200 to 500 Å, and the interlayer spacing (d_{002}) is 3.37 to 3.40 Å. The density (ρ) of such fiber is generally 2.16 to 2.22 g/cm^3.

By controlling the degree of agglutination at 20% or less, the yarn handleability of such pitch-based carbon fiber in producing a composite material can be improved, whereby an excellent carbon fiber reinforced composite material can be produced.

In order to obtain a high thermal conductivity pitch-based carbon fiber having a thermal conductivity of 500 to 1,500 W/m/K or a super-high thermal conductivity pitch-based carbon fiber, the crystalline structure of the carbon fiber, in particular the stack height (Lc 002), should be within a specific range; more specifically, the ratio of stack height (Lc 002)/density (ρ) should be within the range of 120 or more to 500 or less. In case that the ratio of stack height (Lc 002)/density (ρ) is less than 120, the thermal conductivity will not reach 500 W/m/K; in case that the ratio exceeds 500, the compressive strength gets smaller than 0.2 GPa, and the mechanical properties balanced with tensile strength and tensile elastic modulus cannot be obtained.

For furthermore explanation of the super-high thermal conductivity pitch-based carbon fiber of the present invention, the stack height (Lc 002) is generally 260 to 1,000 Å, the layer size (La 110) is 300 to 1,000 Å and the interlayer spacing (d_{002}) is 3.36 to 3.39 Å. The density (ρ) of such fiber is generally 2.18 to 2.24 g/cm^3.

By controlling the degree of agglutination of such pitch-based carbon fiber at 30% or less, the yarn handleability thereof in producing a composite material can be improved, whereby an excellent carbon fiber reinforced composite material can be produced.

It has been found that the high thermal conductivity pitch-based carbon fiber of the present invention can be preferably produced, by infusibilizing the pitch fiber obtained by spinning carbonaceous pitch by routine methods, passing the infusibilized fiber through an oxygen containing atmosphere at a temperature of 300 to 500°C, preferably 350 to 480°C, for an extremely short period of time, to effect a thermal treatment while stretching the fiber at a ratio of 5 to 100%, subsequently passing the fiber through an oxygen containing atmosphere

the maximum temperature of which is 500 to 700 °C, preferably 550 to 650 °C, for a short period of time, to effect pre-carbonization treatment while stretching the fiber at a ratio of 5 to 100%, and subsequently carbonizing the fiber in an inert-gas atmosphere the maximum temperature of which is 2,300 to 3,200 °C, while effecting the stretching process of 1 to 30% if necessary.

According to the production method of the present invention, infusibilized and fragile fiber which has been rendered infusible by heating up to 150 to 350°C, in an oxidative atmosphere following routine methods, is processed, prior to pre-carbonization, in an oxygen-containing atmosphere for a short period of time at a high temperature of 300 to 500 °C. Therefore, the fiber surface is selectively oxidized while the inside of the fiber is progressively polymerized thermally or carbonized at the high-temperature. Consequently, the infusibilized fiber is strengthened, which enables further stretching process of the infusiblized fiber in a furnace for pre-carbonization. Thus, the degree of agglutination of the pre-carbonized fiber is possibly reduced.

It has been found that the carrying out the process of stretching and thermal treatment of the fiber in two stages, namely after the process of infusibilization and during the process of pre-carbonization, the orientation properties of the fiber are improved, and the thermal conductivity there of is particularly increased, so that the fiber with a higher thermal conductivity can be obtained. The process of stretching and thermal treatment in either one of the stages, namely one-stage process of stretching and thermal treatment, cannot produce a high thermal conductivity pitch-based carbon fiber constructed in accordance with the present invention.

It has been found that in order to obtain a super-high thermal conductivity pitch-based carbon fiber having a thermal conductivity of 500 W/m/K or more. the process of stretching and thermal treatment is necessarily carried out in three stages, namely after infusibilization process, during pre-carbonization process, and during carbonization process. The process of stretching and thermal treatment in one stage or two stages cannot produce a pitch-based carbon fiber of super-high thermal conductivity in the above structure.

During the process of stretching and thermal treatment in the first stage after infusibilization process, it is preferable that the oxygen concentration in the oxygen-containing atmosphere is 5 to 80 %; the retention time in a furnace is 1 to 200 seconds (preferably 10 to 100 seconds); and the tension per filament is 0.003 to 0.17 g. During the process of stretching and thermal treatment in the second stage in the process of pre-carbonization after infusibilization, it is preferable that the oxygen concentration in the oxygen-containing atmosphere is 0.01 to 30%; the retention time in a furnace is 20 to 300 seconds (preferably 50 to 200 seconds); and the tension per filament is 0.006 to 0.33 g.

In case that the process of stretching and thermal treatment is required in the third stage of the carbonizing process, the retention time in a furnace during the process of stretching and thermal treatment in the third stage is 1 to 100 minutes (preferably 2 to 60 minutes); and the tension per filament is 0.05 to 20 g.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of producing the pitch-based carbon fiber of the present invention will now be explained in more details.

Carbonaceous pitch can be spun by methods well known to those skilled in the art. Carbonaceous pitch suitable for the production of a pitch-based carbon fiber employing pitch and the like such as petroleum pitch, coal pitch and aromatic hydrocarbons as raw materials, is heated and melted to spin filaments of 1 to 2,000, preferably 50 to 1,000. Treatment oil is given to the individual filaments by using an oiling roller in routine use, whereby a great number of the filaments are bundled, and the filaments in a bundle are then wound as one thread onto a bobbin.

As the treatment oil, there can be used water; alcohols such as ethyl alcohol, isopropyl alcohol, n-propyl alcohol, butyl alcohol, etc.; or dimethyl polysiloxane, alkylphenyl polysiloxane, etc. with a viscosity of 5 to 1,000 cst (at 25 °C), which are diluted with a solvent of a lower boiling point such as silicone oil (polysiloxane) or paraffin oil or are dispersed in water by the addition of emulsifiers; graphite or polyethylene glycol and hindered esters, similarly dispersed; surfactants diluted with water; and other various kinds of treatment oils which are used in common fibers for example polyester fiber and which do not deteriorate pitch fibers.

The amount of treatment oil to be added to a pitch fiber is generally 0.01 to 10 % by weight, and it is specifically 0.05 to 5% by weight preferably.

By simultaneous release of plural bobbins, for example 2 to 50, or the multiple repetition of release and bundling such as step-wise release of the bobbins, for example 2 to 10 at a first time and the remaining portions at next time, the threads of 2 to 50, each composed of a great number of filaments once wound onto one bobbin as has been described above, are bundled (subjected to yarn doubling) to produce a pitch fiber bundle (referred to as "pitch fiber" hereinafter) from 100 to 100,000 filaments, preferably from 500 to 10,000 filaments. The resulting pitch fiber is then wound onto another bobbin.

On considering the infuxibilizing process and pre-carbonization, a heat-resistant treatment oil is put into

the pitch fiber during such bundling. The heat resistant treatment oil is preferably alkylphenyl polysiloxane containing 5 to 80% of phenyl group, more preferably alkylphenyl polysiloxane containing 10 to 50 % of phenyl group. The alkyl group is preferably methyl group, ethyl group and propyl group. Also, two or more species of alkyl groups may be contained in one molecule. There are used those with a viscosity of 10 to 100 cst at 25°C. Antioxidant described hereinbelow may also be added.

As other preferable treatment oils, there may be used dimethyl polysiloxane with an antioxidant added and preferably with a viscosity of 5 to 1,000 cst at 25°C. As the antioxidant, there may be included amines, organic selenium compounds, phenols and the like, such as phenylα-naphthylamine, dilauryl selenide, phenothiazine, and ferric octoate. These antioxidants may possibly be added to the alkylphenyl polysiloxane described above, for the objective to enhance heat resistance.

As preferable treatment oils, there may further be included the individual treatment oils emulsified with surfactants of a boiling point of 600 °C or less. As the surfactants, there may be used polyoxyethylene alkylether, polyoxyethylene alkylester, polyoxyethylene modified silicon, polyoxyalkylene modified silicone and the like.

These treatment oils are added to a pitch fiber at a ratio of 0.01 to 10% by weight, preferably 0.05 to 5% by weight, by means of roller contact, spray coating, foam coating and the like.

By adding a heat resistant treatment oil to the bundled pitch fiber as has been described above, the pitch fiber can acquire remarkably increased strength and distinctively improved yarn handleability.

The pitch fiber thus produced is released from the bobbin and is transferred and fed to an infusibilizing furnace.

The inside of an infusiblizing furnace can be set at a certain predetermined temperature in the range of 150 to 350 °C. It can be set so as to have the temperature gradually elevating from 150°C to 350°C.

The inside of an infusibilizing furnace should be in an oxidative atmosphere. Oxidative gas such as air, oxygen, a mixed gas of air and oxygen, or a mixed gas of air and nitrogen, is fed into an infusibilizing furnace. Oxygen rich gas of an oxygen concentration of 30 to 90% is preferably used as preferable gas.

According to the present invention, no tension is loaded onto a pitch fiber during the infusibilizing process. However, it is preferable to effect the infusibilizing process under the tension of 0.001 to 0.2 g per filament, in order to prevent the occurrence of dragging flaw caused by the dragging of the fiber on the bottom and wall of a furnace due to the deflection of the fiber inside the infusibilizing furnace, and in order to improve the properties of a carbon fiber, such as appearance, tensile strength and tensile elastic modulus.

The infusibilizing process is effected in such fashion that the oxygen concentration in the infusibilized fiber is 7 to 12% by weight.

According to the present invention, the fiber thus infusibilized and containing oxygen of a concentration of 7 to 12% by weight is subjected to a first-stage process of stretching and thermal treatment in an oxygen-containing atmosphere, prior to the process of pre-carbonization in a pre-carbonizing furnace.

The temperature inside of the furnace for the process of stretching and thermal treatment is preferably higher by 100 to 200 °C than the infusibilizing temperature, and generally is a certain fixed temperature in the range of 300 to 500 °C, for example 450 °C. The inside of the furnace may also be set to have the temperature gradient gradually elevating at the inlet to the outlet of the furnace, with the provision that the maximum temperature in such case should not exceed 300 to 500°C. It can possibly be set such that the temperature at the furnace inlet is 350 °C while the temperature at the furnace outlet is 500 °C. If the temperature for the thermal treatment exceeds 500 °C, the infusibilized fiber is unfavorably oxidized too far; if the temperature is less than 300°C, the period of time for thermal treatment is prolonged, or the surface oxidation of the infusibilized fiber gets unsatisfactory. Thus, expected effects can hardly be obtained.

The inside of the furnace for thermal treatment should be in an oxygen-containing atmosphere. Oxidative gas such as air, a mixed gas of air and oxygen, a mixed gas of air and nitrogen, or a mixed gas of nitrogen and oxygen is fed into an infusibilizing furnace. The oxygen concentration is 5 to 80 %, preferably 10 to 50 %. Generally, air is preferably used. In some case, a mixed gas of NOx, SOx, Cl_2 and the like contained in air may be used.

According to the present invention, the retention time of the infusibilized fiber inside the furnace of thermal treatment is 1 to 200 seconds, preferably 10 to 100 seconds. The retention time may be determined, depending on the temperature of thermal treatment. When the retention time exceeds 200 seconds, the infusibilized fiber is unfavorably oxidized too much even if the temperature of thermal treatment is set at 300°C; when the retention time is less than one second, the infusibilized fiber is not oxidized satisfactorily if the temperature of thermal treatment is set at 500°C. Thus, expected effects can hardly be obtained.

According to the present invention, tension is also loaded on the infusibilized fiber during the process of thermal treatment, to effect the stretching treatment of 5 to 100 %. Hence, the tension loaded onto the infusibilized fiber usually is 10 to 500 g per 3,000 filaments, namely 0.003 to 0.17 g per filament.

The stretching may be adjusted by the adjustment of the dimension of tension or by the differential move-

ment of two or more rolls.

According to the process configuration hereinabove mentioned, the infusibilized fiber is oxidized selectively only on the surface thereof, while thermal polymerization of the inside of the fiber by high-temperature is furthermore facilitated, so that the infusibilized fiber composed of a great number of filamments can acquire increased strength. For that reason, the infusibilized fiber is oxidized prior to the pre-carbonization only on the surface of the fiber. Thus, the properties of the carbon fiber as a product are not deteriorated.

According to the present invention, the degree of agglutination of the infusibilized fiber on the surface in a furnace of pre-carbonization is also decreased due to the oxidization of the surface of the infusibilized fiber.

According to the present invention, furthermore, the infusibilized fiber is oxidized selectively only on the surace thereof, while thermal polymerization of the inside of the fiber by high-temperature is facilitated, so that the infusibilized fiber can acquire increased strength. The orientation property of the fiber is further improved by the stretching process of the infusibilized fiber, so the properties of the carbon fiber thus obtained are improved.

The infusibilized fiber thus subjected to the process of thermal treatment and stretching is transferred and fed to a furnace for pre-carbonization, where the process of pre-carbonization, namely a second-stage process of stretching and thermal treatment, is effected in an oxygen-containing atmosphere.

The temperature inside the furnace of pre-carbonization is set so that the maximum temperature should be in the range of 500 to 700 °C. It may be set so as to have the temperature environment elevating step wise from 400°C, 500°C to 600°C, at the inlet to the outlet, the maximum temperature reaching a temperature in the range of 500 to 700°C. If the temperature for thermal treatment is above 700°C, the oxidization of the pre-carbonized fiber progresses too far, unfavorably; if the maximum temperature is less than 500 °C, the period of time for thermal treatment is prolonged or the surface of the pre-carbonized fiber is not satisfactorily oxidized. Thus, expected effects can hardly be obtained.

The inside of the furnace of thermal treatment is maintained in an atmosphere containing oxygen or a lower concentration, by feeding, into the furnace of thermal treatment, inert gas mixed with a small amount of oxygen or air. The concentration of oxygen is 0.01 to 30 %, preferably 0.05 to 10 %. As the inert gas, nitrogen gas or argon gas can be used. Nox, SOx, water vapor, carbonate gas, halogen gas, and the vapor of strong acids may be used as well.

According to the present invention, the retention time of the fiber inside the furnace of pre-carbonization is 20 to 300 seconds, preferably 50 to 200 seconds. The retention time may be determined, depending on the relation between the temperature of the thermal treatment and the oxygen concentration.

If the oxygen content in the atmosphere containing oxygen of a lower concentration is too less such as less than 0.01 %, the surface of the infusibilized fiber cannot effectively be oxidized by heating for a short period of time during the pre-carbonization; if the content exceeds 30 % inversely, it is too much to effect selective oxidation of the surface of the infusibilized fiber even by the thermal treatment for a short period of time, which is disadvantageous in that the inside of the fiber is also oxidized.

When the period of time for the thermal treatment of the infusibilized fiber in the atmosphere containing a lower concentration of oxygen is less than 20 seconds, it is too short to effectively oxidize the surface of the infusibilized fiber even if the oxygen content in the atmosphere is increased; when it exceeds 300 seconds, the period is too long to prevent the oxidation of the inside of the infusibilized fiber even if the oxygen content in the atmosphere is decreased.

According to the present invention, furthermore, tension is loaded onto the fiber to effect the stretching process of 5 to 100 %, concurrently with the thermal treatment. Therefore, the tension generally loaded onto the infusibilized fiber is 20 to 1,000 g per 3,000 filaments, namely 0.006 to 0.33 g per filament. The stretching condition may be set by means of the adjustment of the dimension of the tension or by means of the adjustment of differential movement of two or more rolls.

According to the present invention, the infusibilized fiber is heated and oxidized in the atmosphere containing oxygen of a low concentration in the furnace of pre-carbonization for a short period of time, whereby only the surface of the fiber is selectively oxidized for the strengthening of the surface while the fiber is concurrently carbonized preliminarily, to enable further stretching process of the infusibilized fiber in the furnace of pre-carbonization. Thus, the degree of agglutination of the pre-carbonized fiber is possibly reduced.

As has been mentioned insofar, the process of stretching and thermal treatment carried out in two stages, namely after the infusibilizing process and during the pre-carbonizing process, can reduce the degree of agglutination of the carbon fiber down to 30 %, preferably down to 20% or less. The orientation property of the fiber is simultaneously improved, particularly the thermal conductivity is increased, whereby the fiber of high thermal conductivity is obtained. The process of stretching and thermal treatment in either one of the stages, namely one-stage process of stretching and thermal treatment, cannot produce a pitch-based carbon fiber of high thermal conductivity constructed in accordance with the present invention.

The fiber pre-carbonized in such manner is then transferred and fed to a furnace of carbonization, where the fiber is carbonized in the atmosphere of inert gas the maximum temperature of which is 2,300 to 3,000 °C.

According to the production method described above, there can be obtained a high thermal conductivity pitch-based carbon fiber having a thermal conductivity in the axial direction of fiber of 300 to 500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/density (ρ) of the fiber of 70 to 180, a degree of agglutination of 0 to 20 %, and a compressive strength of 0.3 to 0.5 GPa, as well as a tensile strength of 2.5 to 4.0 GPa and a tensile elastic modulus of 700 to 900 GPa.

According to another embodiment of the present invention, there can be further obtained a super-high thermal conductivity pitch-based carbon fibers having a higher thermal conductivity. In order to obtain such pitch carbon fiber of super-high thermal conductivity, the pre-carbonized fiber produced in the above described manner is transferred and fed to a furnace of carbonization, where the fiber is carbonized while being subjected to the stretching process in the atmosphere of inert gas the maximum temperature of which is 2,600 to 3,200 °C.

For further explanation, the retention time of the fiber in a furnace of carbonization should be 1 to 100 minutes, preferably 2 to 60 minutes. The retention time is determined, depending on the temperature of the thermal treatment.

According to the present embodiment, tension is loaded onto the fiber simultaneously during the carbonization process thereby effecting the stretching process of 1 to 30 %. Thus, the tension loaded onto the fiber is generally 150 to 60,000 g per 3,000 filaments, namely 0.05 to 20 g per filament.

The present embodiment, as the process of stretching and thermal treatment is carried out in three stages, namely after the infusibilizing process, during the pre-carbonizing process, and the stretching process during the carbonization process, it can remarkably improve the orientation property of the fiber, and specifically increase the thermal conductivity distinctively, whereby the fiber of super-high thermal conductivity is obtained. The super-high thermal conductivity pitch-based carbon fiber in the above configuration in accordance with the present invention, cannot be produced by the process of stretching and thermal treatment in one or two stages.

According to the present production method described above, there can be obtained a super-high thermal conductivity pitch-based carbon fiber having a thermal conductivity in the axial direction of fiber of 500 to 1,500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/density (ρ)of the fiber of 120 to 500, a degree of agglutination of 0 to 30 %, and a compressive strength of 0.2 to 0.4 GPa, as well as a tensile strength of 2.5 to 4.5 GP a and a tensile elastic modulus of 700 to 950 GPa.

In the present Description, the properties of the carbon fibers are determined by employing the following measuring methods.

* Thermal conductivity

Thermal conductivity of a carbon fiber was measured by means of laser flash method, by using as a sample the carbon fiber bundle impregnated with epoxy resin.

* X-ray structural parameters

Parameters such as stack height (Lc 002), layer size (La 110), and interlayer spacing (d_{002}), representing the micro structure of a carbon fiber, were determined by X-ray diffraction method.

The stack height (Lc 002) represents the apparent stack height of (002) planes in a crystal of carbon fiber. A larger stack height (Lc 002) is generally regarded as an indication of better crystallinity. The layer size (La 110) represents the apparent layer size in a crystal of carbon fiber. A larger layer size (La 110) is generally regarded as an indication of better crystallinity. Alternatively, the interlayer spacing (d_{002}) represents a interlayer spacing of (002) plane in a crystal of carbon fiber. A smaller interlayer spacing (d_{002}) is generally regarded as an indication of better crystallinity.

After the carbon fibers were ground in a mortar, the stack height (Lc 002), layer size (La 110), and interlayer spacing (d_{002}) of the powdery carbon fibers thus obtained were measured and analyzed according to Gakushinho "Measuring Method for Lattice Constant and Crystalline Size of Artificial Graphite". Based on the following formulas, those parameters were calculated;

$Lc\ 002 = K\lambda/\beta\cos\theta$

$La\ 110 = K\lambda/\beta'\cos\theta'$

$d_{002} = \lambda/2\ \sin\theta$

wherein

$K = 1.0$, $\lambda = 1.5418$ Å

θ : calculated from (002) diffraction angle 2θ

θ': calculated from (110) diffraction angle 2θ

β : FWHM of (002) diffraction pattern calculated with correction;
β′: FWHM of (110) diffraction pattern calculated with correction.

* Density (ρ)

Density (ρ) was measured with a density gradient tube.

* Degree of agglutination

Carbon fiber composed of 3,000 filaments was cut in 1.5 mm-wide sections, which were then immersed in ethanol followed by air spraying for 30 seconds. The total number (N) of the filaments in agglutination was counted under microscopic observation of 20 magnification. Then, the degree of agglutination was determined based on the following formula;

Degree of agglutination = (N/3,000) x 100 (%)

* Compressive strength

A sample of carbon fiber impregnated with epoxy resin was measured according to ASTM D3410.

The method of producing a high thermal conductivity pitch-based carbon fiber in accordance with the present invention will now be explained in examples hereinafter.

Example 1

For producing pitch fiber, carbonaceous pitch containing optically anisotropic phase at the ratio of 45 % and having a softening point of 226 °C, was used as precursor pitch. The precursor pitch was continuously separated into the pitch with more contents of the optically anisotropic phase and the pitch with more contents of optically isotropic phase, which were then individually drawn.

The obtained pitch containing the optically anisotropic phase more, contains 100 % of the optically anisotropic phase. Its softening point was 270 °C and the insoluble part in quinoline was 28.0 % by weight. The pitch for carbon fiber was passed through a melt spinning machine with a spinning nozzle having 500 pores (the pore size of the nozzle, 0.3 mm in diameter), and was spun at 335 °C.

The 500 filaments thus spun were nearly bundled with an air sucker and was then introduced to an oiling roller. By feeding a treatment oil to the filaments at a ratio of about 0.2 % by weight, a pitch fiber composed of 500 filaments was formed. As the treatment oil, methylphenyl polysiloxane of a viscosity of 14 cst at 25 °C was used.

The pitch fiber was wound onto a stainless-steel bobbin of a 210 mm diameter and a 200 mm width, and was spun at a winding velocity of about 500 m/min for 10 minutes. The traverse pitch per one rotation of the bobbin was 10 mm. No break of fiber occurred during the spinning.

Six of the bobbins wound with the pitch fiber were then unwound, and were then bundled while adding a heat-resistance treatment oil by using an oiling roller, to form the pitch fiber composed of 3,000 filaments. Then, the formed fiber was wound onto another stainless bobbin.

As the treatment oil during the bundling, methylphenyl polysiloxane of 40 cst at 25 °C (the content of phenyl group is 45 mol %) was used. The added amount thereof was 0.5 % to the yarn.

While unwinding from the bobbin, the pitch fiber was continuously introduced in linear form into a continuously infusibilizing furnace in oxygen-rich atmosphere (oxygen/nitrogen = 60/40) having such temperature gradient as the furnace inlet temperature of 180 °C and the maximum temperature of 295 °C. The rate of elevating temperature was 6 °C/min, and the period of time for the infusibilizing process was 19 minutes. The tension loaded onto the fiber was 0.007 g per filament which corresponds to 20 g to a fiber composed of 3,000 filaments. The oxygen concentration in the infusibilized fiber after the infusibilizing process was 9.5 % by weight.

During the infusibilizing process, the pitch fiber was smoothly unwound from the bobbin, with no break of the fiber in the infusibilizing furnace. Thus, the infusibilizing process progressed in such smooth manner.

The infusibilized fiber obtained in such manner was fed to the furnace of thermal treatment maintained at 450 °C, prior to the supply thereof to the furnace of pre-carbonization. Tension of 0.007 g per filament was loaded onto the fiber. Air was introduced inside the furnace.

In the above configuration, the period of time required for the thermal treatment of the infusibilized fiber was 25 seconds.

The thermal treatment was smoothly effected with no fiber break in the furnace of thermal treatment. The stretching ratio of the fiber at thermal treatment was 20 %.

The fiber thermally processed in oxygen-containing atmosphere was continuously introduced in linear form into a furnace of pre-carbonization in oxygen-containing atmosphere (oxygen/nitrogen = 5/95) having such temperature gradient as the furnace inlet temperature of 400 °C and the maximum temperature of 600 °C. Tension of 0.017 g per filament was loaded onto the fiber. The stretching ratio was 15 %. The period of time for pre-carbonization was 25 seconds. Continuous treatment was effected for 24 hours, but with no break of the fiber inside the furnace.

The pre-carbonized fiber was heated up to 2,500 °C in argon-gas atmosphere, to obtain carbon fiber. The fiber (filament) diameter was 8.7 μm.

The characteristic properties of the carbon fiber are shown in Table 1.

Example 2

By employing the same materials and method as in Example 1, an infusibilized fiber was produced. As in Example 1, the infusibilized fiber was fed to a furnace of thermal treatment, maintained at 450 °C, prior to the supply thereof to a furnace of pre-carbonization. Tension of 0.007 g per filament was loaded onto the fiber, which was then subjected to thermal treatment for 25 seconds. Air was introduced inside the furnace.

The thermal treatment was smoothly effected with no fiber break in the furnace of thermal treatment. The stretching ratio of the fiber at thermal treatment was 20 %.

The fiber thermally processed in oxygen-containing atmosphere was continuously introduced in linear form into a furnace of pre-carbonization in oxygen-containing atmosphere (oxygen/nitrogen = 5/95) having such temperature gradient as the furnace inlet temperature of 400 °C and the maximum temperature of 600 °C. Differently from Example 1, tension of 0.067 g per filament was loaded onto the fiber. The stretching ratio was 19%. The period of time for pre-carbonization was 25 seconds. Continuous treatment was effected for 24 hours, but without any break of fiber inside the furnace.

The pre-carbonized fiber was heated up to 2,800 °C in argon-gas atmosphere, to obtain carbon fiber. The fiber (filament) diameter was 8.4 μm.

The characteristic properties of the carbon fiber are shown in Table 1.

Table 1

	First-Stage Stretching and Thermal Treatment			Second-Stage Stretching and Thermal Treatment			Carbonization Process	Properties of Carbon Fiber				Properties of Carbon Fiber		
	Maximum Temp.	Tension g/filament	Stretching ratio %	Maximum Temp.	Tension g/filament	Stretching ratio %	Maximum Temp.	Thermal Conductivity W/m/K	Lc 002/ σ	Degree of Agglutination %	Compressive Strength GPa	Tensile Strength GPa	Tensile Elastic Modulus GPa	Filer Diameter μm
Example 1	450	0.007	20	600	0.017	15	2,500	340	97	9	0.42	3.7	720	8.7
Example 2	450	0.007	20	600	0.067	19	2,800	450	136	12	0.34	3.8	840	8.4
Comparative Example 1	-	-	-	900	0.017	15	2,500	230	66	23	0.42	3.1	610	9.5
Comparative Example 2	450	0.007	20	-	-	-	2,500	210	63	16	0.43	3.0	590	9.2

Comparative Example 1

By employing the same materials and method as in Example 1, an infusibilized fiber was produced. Without effecting the thermal treatment of the infusibilized fiber prior to pre-carbonization, the infusibilized fiber was directly introduced in linear form continuously to a furnace of pre-carbonization in oxygen-containing atmosphere (oxygen/nitrogen = 5/95) for pre-carbonization. The furnace of pre-carbonization had such temperature gradient as the furnace inlet temperature of 400°C and the maximum temperature of 900°C. The process of pre-carbonization was continued over 250 seconds. Tension of 0.017 g per filament was loaded onto the fiber. The stretching ratio then was 15 %.

The pre-carbonized fiber was heated up to 2,500 °C in argon-gas atmosphere, to obtain carbon fiber. The fiber (filament) diameter was 9.5 μm.

The characteristic properties of the carbon fiber are shown in Table 1.

Comparative Example 2

By employing the same materials and method as in Example 1, an infusibilized fiber was produced. As in Example 1, the infusibilized fiber was fed to a furnace of thermal treatment, maintained at 450 °C. Tension of 0.007 g per filament was loaded onto the fiber, which was then subjected to thermal treatment for 25 seconds. Air was introduced inside the furnace. The fiber stretching ratio at the thermal treatment was 20 %.

Differently from Example 1, the fiber thermally processed in oxygen-containing atmosphere was directly heated up to 2,500 °C in argon-gas atmosphere, to obtain carbon fiber. The fiber (filament) diameter was 9.2 μm.

The characteristic properties of the carbon fiber are shown in Table 1.

Example 3

By employing the same materials and method as in Example 1, a pre-carbonized fiber was produced.

The pre-carbonized fiber was continuously fed in linear form to a furnace of carbonization in argon-gas atmosphere at the maximum temperature of 2,800 °C. Tension of 0.3 g per filament was loaded onto the fiber. The stretching ratio was 9 %. The period of time for carbonization was 10 minutes. The fiber (filament) diameter was 8.3 μm.

The characteristic properties of the carbon fiber are shown in Table 2.

Example 4

By employing the same materials and method as in Example 1, an infusibilized fiber was produced. As in Example 1, the infusibilized fiber was fed to a furnace of thermal treatment maintained at 450 °C, prior to the supply thereof to a furnace of pre-carbonization. Tension of 0.007 g per filament was loaded onto the fiber, which was then subjected to thermal treatment for 25 seconds. Air was introduced inside the furnace.

The thermal treatment was smoothly effected with no fiber break in the furnace of thermal treatment. The stretching ratio of the fiber at thermal treatment was 20 %.

The fiber thermally processed in oxygen-containing atmosphere was continuously introduced in linear form into a furnace of pre-carbonization in oxygen-containing atmosphere (oxygen/nitrogen = 5/95) having such temperature gradient as the furnace inlet temperature of 400 °C and the maximum temperature of 600 °C. Differently from Example 1, tension of 0.067 g per filament was loaded onto the fiber. The stretching ratio was then 19%. The period of time for pre-carbonization was 25 seconds. Continuous treatment was effected for 24 hours, but with no break of fiber inside the furnace.

The pre-carbonized fiber was continuously introduced in linear form to a furnace of carbonization in argon-gas atmosphere at the maximum temperature of 3,000 °C. Tension of 0.4 g per filament was loaded onto the fiber. The stretching ratio was 10 %. The period of time for carbonization was 12 minutes. The fiber (filament) diameter was 8.1 μm.

The characteristic properties of the carbon fiber are shown in Table 2.

Table 2

	First-Stage Stretching and Thermal Treatment			Second-Stage Stretching and Thermal Treatment			Drawing and Carbonization Process			Properties of Carbon Fiber						
	Maximum Temp.	Tension g/filament	Stretching ratio %	Maximum Temp.	Tension g/filament	Stretching ratio %	Maximum Temp.	Tension g/filament	Stretching ratio %	Thermal Conductivity W/m/K	Lc 002/ 0	Degree of Agglutination %	Compressive Strength GPa	Tensile Strength GPa	Tensile Elastic Modulus GPa	Filer Diameter µm
Example 3	450	0.007	20	600	0.017	15	2,800	0.3	9	570	145	17	0.31	3.9	870	8.3
Example 4	450	0.007	20	600	0.067	19	3,000	0.4	10	1040	320	21	0.26	3.7	910	8.1
Comparative Example 3	-	-	-	900	0.017	15	2,800	0.3	8	480	110	42	0.30	3.2	730	9.1

Comparative Example 3

By employing the same materials and method as in Example 1, an infusibilized fiber was produced. Without effecting the thermal treatment of the infusibilized fiber prior to pre-carbonization, the infusibilized fiber was directly introduced in linear form continuously to a furnace of pre-carbonization in oxygen-containing atmosphere (oxygen/nitrogen = 5/95) for pre-carbonization. The furnace of pre-carbonization had such temperature gradient as the furnace inlet temperature of 400°C and the maximum temperature of 900°C. The process of pre-carbonization was continued over 250 seconds. Tension of 0.017 g per filament was loaded onto the fiber. The stretching ratio then was 15 %.

The pre-carbonized fiber was continuously introduced into a furnace of carbonization at the maximum temperature of 2,800 °C in argon-gas atmosphere. Tension of 0.3 g per filament was loaded onto the fiber. The stretching ratio was 8 %. The period of time for carbonization was 10 minutes. The fiber (filament) diameter was 9.1 μm.

The characteristic properties of the carbon fiber are shown in Table 2.

Effects of the Invention:

As has been described above, the high thermal conductivity pitch-type carbon fiber in accordance with the present invention has characteristic features, such that the thermal conductivity is extremely high without causing deterioration of the tensile strength and tensile elastic modulus thereof, that the compressive strength is also high, and that the yarn handleability is excellent.

Claims

1. A high thermal conductivity pitch-based carbon fiber characterized by having a thermal conductivity in the axial direction of fiber of 300 to 1,500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/ density (ρ) of 70 to 500, a degree of agglutination of 0 to 30 %, and a compressive strength of 0.2 to 0.5 GPa.

2. A high thermal conductivity pitch-based carbon fiber according to claim 1, having a tensile strength of 2.5 to 4.5 GPa and a tensile elastic modulus of 700 to 950 GPa.

3. A method of producing a high thermal conductivity pitch-based carbon fiber, comprising the steps of:
infusibilizing the pitch fiber obtained by spinning carbonaceous pitch;
passing the infusibilized fiber for 1 to 200 seconds through an oxygen containing atmosphere at a temperature of 300 to 500°C to effect a thermal treatment while stretching the fiber at a ratio of 5 to 100%;
subsequently passing the fiber for 20 to 300 seconds through an oxygen containing atmosphere the maximum temperature of which is 500 to 700°C to effect a pre-carbonization while stretching the fiber at a ratio of 5 to 100 %; and then
carbonizing the fiber in an inert-gas atmosphere the maximum temperature of which is 2,300 to 3,200 °C, while stretching the fiber at a ratio of 1 to 30 % if necessary.

4. A high thermal conductivity pitch-based carbon fiber according to claim 1, characterized by having a thermal conductivity in the axial direction of fiber of 300 to 500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/density (ρ) of 70 to 180, a degree of agglutination of 0 to 20 %, and a compressive strength of 0.3 to 0.5 GPa.

5. A high thermal conductivity pitch-based carbon fiber according to claim 4, having a tensile strength of 2.5 to 4.0 GPa and a tensile elastic modulus of 700 to 900 GPa.

6. A method of producing a high thermal conductivity pitch-based carbon fiber according to claim 4, comprising the steps of:
infusibilizing the pitch fiber obtained by spinning carbonaceous pitch;
passing the infusibilized fiber for 1 to 200 seconds through an oxygen containing atmosphere at a temperature of 300 to 500°C to effect a thermal treatment while stretching the fiber at a ratio of 5 to 100%;
subsequently passing the fiber for 20 to 300 seconds through an oxygen containing atmosphere the maximum temperature of which is 500 to 700°C to effect a pre-carbonization while stretching the fiber

at a ratio of 5 to 100%; and then

carbonizing the fiber in an inert-gas atmosphere the maximum temperature of which is 2,300 to 3,000 °C.

7. A high thermal conductivity pitch-based carbon fiber according to claim 1, characterized by having a thermal conductivity in the axial direction of fiber of 500 to 1,500 W/m/K, a ratio of stack height (Lc 002) of the crystalline structure of the fiber/density (ρ) of 120 to 500, a degree of agglutination of 0 to 30 %, and a compressive strength of 0.2 to 0.4 GPa.

8. A high thermal conductivity pitch-type carbon fiber according to claim 7, having a tensile strength of 2.5 to 4.5 GPa and a tensile elastic modulus of 700 to 950 GPa.

9. A method of producing a high thermal conductivity pitch-based carbon fiber according to claim 7, comprising the steps of:

infusibilizing the pitch fiber obtained by spinning carbonaceous pitch;

passing the infusibilized fiber for 1 to 200 seconds through an oxygen containing atmosphere at a temperature of 300 to 500°C to effect a thermal treatment while stretching the fiber at a ratio of 5 to 100%;

subsequently passing the fiber for 20 to 300 seconds through an oxygen containing atmosphere the maximum temperature of which is 500 to 700°C to effect a pre-carbonization while stretching the fiber at a ratio of 5 to 100%; and then

carbonizing the fiber in an inert-gas atmosphere the maximum temperature of which is 2,600 to 3,200°C, while stretching the fiber at a ratio of 1 to 30%.