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(54) NONWOVEN FABRIC, FELT AND MANUFACTURING METHOD THEREOF

(57) A nonwoven fabric which contains pitch-based carbon fibers having a high elongation and a high elastic modulus which are not attained in the prior art and is obtained by improving the tensile elongation which was defect of carbon fibers derived from mesophase pitch, a felt obtained from the nonwoven fabric, and production processes therefor.

The nonwoven fabric contains pitch-based carbon fibers, wherein the pitch-based carbon fibers have (i) an average fiber diameter (D1) measured by an optical microscope of more than 2 μm and 20 μm or less, (ii) a percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) measured by an optical microscope of 3 to 20 %, (iii) a tensile elastic modulus of 80 to 300 GPa and (iv) a tensile elongation of 1.4 to 2.5 %.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a nonwoven fabric containing pitch-based carbon fibers having a high elongation and a high elastic modulus, a felt and a heat insulating material obtained from the nonwoven fabric, and production processes therefor. More specifically, it relates to a nonwoven fabric containing pitch-based carbon fibers which are obtained from mesophase pitch and stabilized and baked under specific conditions and a felt and a heat insulating material which are obtained from the nonwoven fabric and have excellent durability and oxidation resistance.

BACKGROUND ART

[0002] Carbon fibers obtained from polyacrylonitrile have well-balanced strength and elastic modulus and are widely used in structural members for industrial robot arms and airplanes. To further expand the application of the carbon fibers in auto members, their cost must be reduced. However, the starting material of the carbon fibers obtained from polyacrylonitrile is a synthetic resin and there is limitation to the reduction of cost.

[0003] As inexpensive carbon fibers, there are pitch-based carbon fibers obtained from pitch which is oil or coal residue. The pitch-based carbon fibers are roughly divided into carbon fibers obtained from isotropic pitch and carbon fibers obtained from mesophase pitch.

[0004] The pitch-based carbon fibers obtained from isotropic pitch have a high elongation of more than 2 % as described, for example, in Patent Document 1. However, carbon fibers having a low degree of graphitization and a high elastic modulus cannot be obtained. Meanwhile, the carbon fibers obtained from mesophase pitch can easily achieve a high elastic modulus due to their high degree of graphitization. However, although a high elastic modulus can be achieved due to the growth of graphite crystals caused by high-temperature baking, elongation degrades with the result of reduced strength. Therefore, it has been extremely difficult to produce pitch-based carbon fibers having a high elongation and a high elastic modulus.

[0005] As means for solving these problems, a method of modifying raw material pitch is proposed. For example, Patent Document 2 proposes a raw material which has a hydrogen/carbon atomic ratio of 0.5 to 0. 7, contains oriented carbon in an amount of 50 % or less based on the total of all the aromatic carbon atoms, 5 to 60 % of anisotropic spheres having a diameter of 5 to 150 μm and 25 wt% or less of pyridine-insoluble matter and is obtained by polymerizing a condensation polycyclic hydrocarbon at 100 to 400°C in the presence of hydrogen fluoride and boron trifluoride to obtain pitch having an optical anisotropy content of less than 5 % and thermally polymerizing the pitch at 250 to 450°C. However, since strong acids such as hydrogen fluoride and boron trifluoride are used as catalysts, special equipment must be used and the disposal of waste acids extracted after a reaction costs dear.

[0006] Patent Document 3 proposes a process for producing carbon fibers from a reaction product obtained by reacting mesophase pitch with a crosslinking agent. However, since a special crosslinking agent is used even in this process, the process becomes costly.

[0007] As an alternative for improving the strength of pitch-based carbon fibers, Patent Document 4 discloses a process for producing pitch-based carbon fibers by containing iodine in pitch fibers in the absence of oxygen and heating them in an inert atmosphere. However, this process has a disadvantage that iodine adsorbed to the pitch in the carbonization step is desorbed with the result that the service life of a furnace is significantly shortened.

[0008] Patent Document 5 proposes a process in which carbon fiber precursors obtained by spinning are stabilized, the obtained pitch-based stabilized fibers are heated at 700°C or lower in an inert atmosphere under tension, and the stabilized fibers are carbonized and graphitized in an inert atmosphere under no tension. Although this process can be employed when the carbon fiber precursors are long fibers, it cannot be employed, for example, for carbon fiber precursors formed by the melt blowing method as they become a nonwoven fabric.

[0009] Patent Document 6 introduces a process for producing carbon fibers having improved strength by carrying out stabilization at 100 to 400°C in an oxidative atmosphere containing 0.1 to 40 vol% of NO_2 and 4 to 40 vol% of H_2O. However, in this process, the elastic modulus lowers as shown in Examples.

[0010] As described above, it has been extremely difficult to produce pitch-based carbon fibers having a high elongation and a high elastic modulus.

(Patent Document 1) JP-A 2-169727
(Patent Document 2) JP-A 9-279154
(Patent Document 3) JP-A 1-207420
(Patent Document 4) JP-A 8-27628
(Patent Document 5) JP-A 62-69826
(Patent Document 6) JP-A 2-6618

DISCLOSURE OF THE INVENTION

[0011] Carbon fibers obtained from mesophase pitch have a problem that they have a low tensile elongation as compared with carbon fibers obtained from isotropic pitch though they have an excellent elastic modulus, thereby making it difficult to use them in structural members for industrial robot arms and airplanes.

[0012] It is therefore an object of the present invention to provide a nonwoven fabric containing pitch-based carbon fibers having a high elongation and a high elastic modulus which cannot be attained in the prior art by improving the tensile elongation of carbon fibers derived from mesophase pitch. It is another object of the present invention to provide a felt obtained by needle punching a nonwoven fabric containing pitch-based carbon fibers having a high elongation and a high elastic modulus and a heat insulating material obtained from the felt.

[0013] The inventors of the present invention have found that stabilized fibers containing 8 to 15 wt% of oxygen are produced and baked at 800 to 1,800°C in the stabilization step of a process for producing carbon fibers from mesophase pitch so as to obtain a nonwoven fabric containing pitch-based carbon fibers having an improved tensile elongation and a high elongation and a high elastic modulus which cannot be attained in the prior art. The present invention has been accomplished based on this finding.

[0014] That is, the present invention includes the following inventions.

1. A nonwoven fabric containing pitch-based carbon fibers, wherein the pitch-based carbon fibers have (i) an average fiber diameter (D1) measured by an optical microscope of more than 2 μm and 20 μm or less, (ii) a percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) measured by an optical microscope of 3 to 20 %, (iii) a tensile elastic modulus of 80 to 300 GPa and (iv) a tensile elongation of 1.4 to 2.5 %.
2. The nonwoven fabric of the above paragraph 1, wherein the pitch-based carbon fibers have a tensile elastic modulus of 100 to 300 GPa and a tensile elongation of 1.5 to 2.4 %.
3. The nonwoven fabric of the above paragraph 1, wherein the average fiber diameter (D1) measured by an optical microscope of the pitch-based carbon fibers is more than 10 μm and 20 μm or less.
4. The nonwoven fabric of the above paragraph 1 which has a tensile strength of 10 N/5 cm piece or more.
5. A process for producing a nonwoven fabric, comprising the steps of:

    (1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors;
    (2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including carbon fibers containing 8 to 15 wt% of oxygen; and
    (3) baking the stabilized web at 800 to 1,800°C.

6. The production process of the above paragraph 5, wherein spinning is carried out by a melt blowing method.
7. The production process of the above paragraph 5, wherein the average fiber length of the carbon fiber precursors of the precursor web is 4 to 25 cm.
8. The production process of the above paragraph 5, wherein the amount of oxygen added to the carbon fibers of the stabilized web is 9 to 12 wt%.
9. The production process of the above paragraph 5, wherein the fiber length retention (%) defined by the following equation (I) before and after baking is 90 % or more.

$$\text{Fiber length retention} = 100 \times L^1/L^0 \qquad \text{(I)}$$

L^0: fiber length before baking
L^1: fiber length after baking

10. A felt obtained by needle punching the nonwoven fabric of the above paragraph 1.
11. The felt of the above paragraph 10 which has a delamination strength in the thickness direction of 0.25 N/5 cm piece or more.
12. The felt of the above paragraph 10, wherein the carbon fibers have an average fiber diameter of more than 10 μm and 20 μm or less and a weight of 250 to 1,000 g/m^2.
13. A graphitized felt obtained by further heating the felt of the above paragraph 10 at 2,000 to 3,500°C.
14. A process for producing a felt, comprising the steps of:

    (1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors;
    (2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including carbon

fibers containing 8 to 15 wt% of oxygen;
(3) baking the stabilized web at 800 to 1,800°C to produce a nonwoven fabric; and
(4) needle punching the nonwoven fabric.

15. The production process of the above paragraph 14, wherein the nonwoven fabric is punched 15 to 100 times/cm^2 with a needle having a barb depth of 0.15 mm or more.
16. A composite obtained by impregnating the felt of the above paragraph 10 with a resin.
17. A composite obtained by impregnating the graphitized felt of the above paragraph 13 with a resin.
18. A heat insulating material obtained by heating the composite of the above paragraph 16 at 500 to 2,200°C.
19. A process for producing a heat insulating material, comprising the steps of:

(1) impregnating the felt of the above paragraph 10 with a resin to produce a composite; and
(2) heating the composite at 500 to 2,200°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Fig. 1 is a schematic diagram of the barb portion of a needle; and
Fig. 2 is a schematic diagram of the needle.

Explanation of letters or notations

[0016]

1	Depth of barb
2	height of kick-up
3	felt
4	needle
5	bed plate
6	barb at the shortest distance from distal end (first barb)
7	depth of needle
8	interval between adjacent barbs

BEST MODE FOR CARRYING OUT THE INVENTION

[nonwoven fabric]

[0017] The present invention is a nonwoven fabric containing pitch-based carbon fibers. The pitch-based carbon fibers constituting the nonwoven fabric have (i) an average fiber diameter (D1) measured by an optical microscope of more than 2 μm and 20 μm or less, (ii) a percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) measured by an optical microscope of 3 to 20 %, (iii) a tensile elastic modulus of 80 to 300 GPa, and (iv) a tensile elongation of 1.4 to 2.5 %.

(carbon fibers: tensile elastic modulus and tensile elongation)

[0018] The mechanical properties of the carbon fibers greatly change according to their baking temperature. Therefore, the tensile elastic modulus and tensile elongation of the carbon fibers greatly change by their heat history in the production process of the carbon fibers. For example, carbon fibers obtained from isotropic pitch can achieve an elongation of more than 1.4 % at a wide temperature range from a low temperature to a high temperature. However, the elastic modulus of the carbon fibers hardly exceeds 50 GPa. On the other hand, carbon fibers obtained from mesophase pitch can achieve an elastic modulus of more than 80 GPa by setting the baking temperature to 800°C or higher. However, in the conventional production process, the elongation of the carbon fibers becomes less than 1.4 %. When the baking temperature is lower than 800°C, it is impossible to achieve an elastic modulus of 80 GPa. As described above, it has been difficult to obtain pitch-based carbon fibers having a tensile elastic modulus of 80 to 300 GPa and a tensile elongation of 1.4 to 2.5 % in the prior art.

[0019] The feature of the present invention is that pitch-based carbon fibers having a high tensile elongation and a high elastic modulus which cannot be attained in the prior art are manufactured by producing stabilized fibers containing 8 to 15 wt% of oxygen and baking the stabilized fibers at 800 to 1, 800°C in the stabilization step of a process for producing pitch-based carbon fibers from mesophase pitch.

[0020] The tensile elastic modulus of the pitch-based carbon fibers constituting the nonwoven fabric of the present invention is 80 to 300 GPa, preferably 100 to 300 GPa, more preferably 180 to 300 GPa. The tensile elongation of the pitch-based carbon fibers constituting the nonwoven fabric of the present invention is 1.4 to 2.5 %, preferably 1.5 to 2.4 %, more preferably 1.6 to 2.3 %. Therefore, the pitch-based carbon fibers constituting the nonwoven fabric of the present invention have preferably a tensile elastic modulus of 100 to 300 GPa and a tensile elongation of 1.5 to 2.4 %, more preferably a tensile elastic modulus of 180 to 300 GPa and a tensile elongation of 1.6 to 2.3 %. (carbon fibers: average fiber diameter (D1) and degree of fiber diameter distribution (S1))

[0021] The pitch-based carbon fibers constituting the nonwoven fabric of the present invention have a specific average fiber diameter (D1) and a specific percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) in order to set their tensile elastic modulus and tensile elongation to the above ranges.

[0022] The average fiber diameter (D1) measured by an optical microscope of the pitch-based carbon fibers constituting the nonwoven fabric of the present invention is more than 2 μm and 20 μm or less. When the average fiber diameter is more than 10 μm and 20 μm or less, the pitch-based carbon fibers become excellent in oxidation resistance and strength advantageously. The average fiber diameter is more preferably more than 10 μm and 15 μm or less.

[0023] The percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) measured by an optical microscope of the pitch-based carbon fibers constituting the nonwoven fabric of the present invention is 3 to 20 %, preferably 5 to 15 %, more preferably 8 to 13%.

(tensile strength of nonwoven fabric)

[0024] The tensile strength of the nonwoven fabric of the present invention is preferably 10 N/5 cm piece or more, more preferably 12 N/5 cm piece or more. When the tensile strength of the nonwoven fabric is 10 N/5 cm piece or more, the tensile strength of a felt obtained by molding such as needle punching improves. This felt can be used in heat insulating materials and acoustic insulating materials. The tensile strength of the nonwoven fabric is a value obtained when a sample having a width of 5 cm and a length of 20 cm is pulled in the lengthwise direction with a Tensilon measuring instrument.

[process for producing nonwoven fabric]

[0025] The nonwoven fabric of the present invention can be manufactured by (1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors [step (1)], (2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including carbon fibers containing 8 to 15 wt% of oxygen [step (2)] and (3) baking the stabilized web at 800 to 1, 800°C [step (3)]. The nonwoven fabric of the present invention containing pitch-based carbon fibers having a high elongation and a high elastic modulus can be obtained by this process.

[0026] A description is subsequently given of each step of the present invention.

(step (1): spinning)

[0027] Mesophase pitch is preferred as the raw material of the pitch-based carbon fibers. The mesophase content of the mesophase pitch is preferably 90 % or more, more preferably 95 % or more, much more preferably 99 % or more. The mesophase content of the mesophase pitch can be confirmed by observing molten pitch through a polarization microscope. Examples of the raw material of the mesophase pitch include condensation polycyclic hydrocarbon compounds such as naphthalene and phenanthrene, and condensation heterocyclic compounds such as petroleum-based pitch and coal-based pitch. Out of these, condensation polycyclic hydrocarbon compounds such as naphthalene and phenanthrene are preferred.

[0028] The softening point of the raw material pitch is preferably 230°C to 340°C. The stabilization of the carbon fiber precursors must be carried out at a temperature lower than the softening point. Therefore, when the softening point is lower than 230°C, stabilization must be carried out at a temperature lower than at least the softening point with the result that stabilization takes long disadvantageously. When the softening point is higher than 340°C, the thermal decomposition of the pitch tends to occur, thereby causing a problem such as the formation of air bubbles in yarn by the generated gas disadvantageously. The softening point is more preferably 250 to 320°C, much more preferably 260 to 310°C. The softening point of the raw material pitch can be obtained by the Mettler method. The raw material pitches may be used in combination of two or more. Preferably, the raw material pitch to be combined has a mesophase content of at least 90 % and a softening point of 230°C to 340°C.

[0029] The step [1] is to produce a precursor web containing carbon fiber precursors by spinning mesophase pitch. The spinning method is not particularly limited but a so-called "melt spinning method" may be employed. Stated more specifically, an ordinary spinning stretching method in which mesophase pitch delivered from a spinneret is taken up by a winder, a melt blowing method in which hot air is used as an atomizing source and a centrifugal spinning method in which mesophase pitch is taken up by making use of centrifugal force may be employed. Out of these, the melt blowing method is desirably used from the viewpoints of the control of the carbon fiber precursors and high productivity.

[0030] A description is subsequently given of the melt blowing method. In the present invention, a spinning nozzle for forming carbon fiber precursors may have any shape. A spherical spinning nozzle is generally used but an atypical nozzle such as an elliptic nozzle may be used. The (LN/DN) ratio of the length (LN) to the hole diameter (DN) of a nozzle hole is preferably 2 to 20. When LN/DN is more than 20, strong shear force is applied to mesophase pitch passing through the nozzle, thereby forming a radial structure on the section of the fiber. The formation of the radial structure may crack the section of the fiber in the baking step, whereby mechanical properties may be deteriorated disadvantageously. When LN/DN is less than 2, shear force cannot be applied to the raw material pitch with the result that carbon fiber precursors which are little oriented are obtained. Therefore, even when the carbon fiber precursors are baked, they cannot have excellent mechanical properties disadvantageously.

[0031] To obtain excellent mechanical properties, appropriate shear force must be applied to mesophase pitch. Therefore, the (LN/DN) ratio of the length (LN) to the hole diameter (DN) of the nozzle hole is preferably 2 to 20, particularly preferably 3 to 12. The temperature of the nozzle at the time of spinning, the shear speed when the mesophase pitch passes through the nozzle, the amount of air blown from the nozzle and the temperature of air are not particularly limited and a condition under which a stable spinning state can be maintained, that is, the melt viscosity of the mesophase pitch in the nozzle hole should be 1 to 100 Pa·s.

[0032] When the melt viscosity of the mesophase pitch passing through the nozzle is less than 1 Pa·s, the melt viscosity is too low, thereby making it impossible to maintain the shape of yarn disadvantageously. When the melt viscosity of the mesophase pitch is higher than 100 Pa·s, strong shear force is applied to the mesophase pitch, thereby forming the radial structure on the section of the fiber disadvantageously. To set shear force to be applied to the mesophase pitch to an appropriate range and maintain the shape of the fiber, the melt viscosity of the mesophase pitch passing through the nozzle must be controlled. Therefore, the melt viscosity of the mesophase pitch is set to preferably 1 to 100 Pa·s, more preferably 3 to 30 Pa·s, much more preferably 5 to 25 Pa·s.

[0033] The carbon fibers constituting the nonwoven fabric of the present invention have an average fiber diameter (D1) of more than 2 μm and 20 μm or less. The average fiber diameter of the carbon fibers can be controlled by changing the hole diameter of the nozzle, the delivery rate of the raw material pitch from the nozzle or the draft ratio. The draft ratio can be changed by blowing a gas having a linear velocity of 100 to 20,000 m/min and heated at 100 to 400°C to a portion near the thinning point. The gas to be blown is not particularly limited but desirably air from the viewpoints of cost performance and safety.

[0034] The carbon fiber precursors are captured on a belt such as a metal net to become a precursor web. At this point, the weight of the web can be controlled to any value by the conveyance speed of the belt but the carbon fiber precursors may be formed into a laminate by crosslapping as required. The weight of the precursor web is preferably 150 to 1,000 g/m^2 in consideration of productivity and process stability.

[0035] The average fiber length of the carbon fiber precursors is preferably 4 to 25 cm. When the average fiber length of the carbon fiber precursors is less than 4 cm, the strength of the precursor web captured on a belt such as a metal net greatly lowers, thereby making it difficult to form a laminate by crosslapping and reducing productivity disadvantageously. When the average fiber length is more than 25 cm, the precursor web becomes too bulky, thereby making it difficult to remove a reaction heat produced by a reaction between the precursor web and an oxidizing gas in the subsequent stabilization step. Thereby, the precursor web may be reduced to ashes disadvantageously. The average fiber length of the carbon fiber precursors is more preferably 5 to 10 cm.

[0036] The average fiber diameter of the carbon fiber precursors obtained by spinning is more than 2 μm and 20 μm or less. When the average fiber diameter is 2 μm or less, the control of the amount of oxygen is difficult in the step of producing stabilized fibers containing 8 to 15 wt% of oxygen from the carbon fiber precursors. Therefore, the quality of carbon fibers obtained by baking cannot be stabilized and also the carbon fiber precursors are reduced to ashes by the reaction heat of stabilization. When the average fiber diameter is more than 20 μm, it takes a huge amount of time to manufacture stabilized fibers containing more than 8 wet% of oxygen in the step of manufacturing stabilized fibers containing 8 to 15 wt% of oxygen from the carbon fiber precursors, thereby greatly reducing productivity disadvantageously. The average fiber diameter of the carbon fiber precursors is more preferably more than 10 μm and 20 μm or less, much more preferably more than 10 μm and 15 μm or less.

[0037] The percentage of the degree of fiber diameter distribution (S1) to average fiber diameter of the carbon fiber precursors is preferably 3 to 20 %. The CV value is an index for variations in fiber diameter. As the CV value becomes smaller, the process stability becomes higher and the variations become smaller. However, to manufacture carbon fiber precursors having a CV value of less than 3 %, changes in the amount of a resin delivered from the capillaries of the spinneret must be controlled as much as possible. Therefore, the spinneret is made small with the result of a great reduction in productivity due to the reduction of the number of capillaries. When the CV value is larger than 20 %, it is difficult to control the amount of oxygen in the step of manufacturing stabilized fibers containing 7 to 15 wt% of oxygen from the carbon fiber precursors with the result that the quality of pitch-based carbon fibers obtained by baking cannot be stabilized disadvantageously. The CV value is more preferably 8 to 15 %.

(step (2): stabilization)

[0038] The step (2) is to manufacture a stabilized web including carbon fibers containing 8 to 15 wt% of oxygen by stabilizing the precursor web in an oxidative gas atmosphere.

[0039] The present invention is characterized in that the amount of oxygen added to the stabilized fibers obtained in step (2) is 8 to 15 wt%. When the amount of oxygen added to the stabilized fibers is less than 8 wt%, the tensile elongation of the carbon fibers obtained by baking in the step (3) cannot exceed 1.4%. When the amount of oxygen added to the carbon fibers is more than 15 wt%, an excellent elastic modulus which is the feature of pitch-based carbon fibers obtained from mesophase pitch is greatly reduced disadvantageously. The amount of oxygen which is preferred for obtaining a high tensile elongation and a high elastic modulus is preferably 8 to 13 wt%, particularly preferably 9 to 12 wt%.

[0040] The stabilization of the carbon fiber precursors is carried out in an oxidative gas atmosphere. The term "oxidative gas" as used herein refers to air or a mixed gas of air and a gas which can extract an electron from the carbon fiber precursors. Examples of the gas capable of extracting an electron from the carbon fiber precursors include ozone, iodine, bromine and oxygen. However, when safety, convenience and cost performance are taken into consideration, the carbon fiber precursors are particularly preferably stabilized in the air.

[0041] The carbon fiber precursors may be stabilized in either a batch manner or a continuous manner, preferably a continuous manner when productivity is taken into account. The stabilization temperature is preferably 150 to 350°C, more preferably 160 to 340°C. In the batch manner, the temperature elevation rate is preferably 1 to 10°C/min. The temperature elevation rate is more preferably 3 to 9°C/min in consideration of productivity and process stability. In the case of the continuous manner, the temperature elevation rate can be achieved by letting the carbon fiber precursors passing through a plurality of reaction chambers which are each set to an arbitrary temperature. To let the carbon fiber precursors pass through a plurality of reaction chambers sequentially, a conveyor may be used. The amount of oxygen added to the stabilized fibers greatly depends on the temperature of a furnace and residence time in the furnace. In the continuous manner, the amount of oxygen added to the pitch-based stabilized yarn is preferably set to 8 to 15 wt% by controlling the speed of the conveyor and the temperature of each reaction chamber to adjust the residence time in each reaction chamber. The speed of the conveyor which depends on the number and sizes of reaction chambers is preferably 0.1 to 1.5 m/min.

(step (3): baking)

[0042] The step (3) is to obtain a nonwoven fabric by baking the stabilized web at 800 to 1,800°C.

[0043] The stabilized web is baked in vacuum or a non-oxidative atmosphere using an inert gas such as nitrogen, argon or krypton to become a nonwoven fabric. The baking is preferably carried out at normal pressure in a nitrogen atmosphere in consideration of cost. It may be carried out in either a batch manner or a continuous manner, preferably a continuous manner in consideration of productivity.

[0044] The fiber length retention (%) defined by the following equation (I) can be set to 90 % or more in the baking step by adjusting the amount of oxygen added to the stabilized fibers to 8 to 15 wt% in the step (2) in the process of the present invention.

$$\text{Fiber length retention} = 100 \times L^1/L^0 \qquad \text{(I)}$$

L^0: fiber length before baking
L^1: fiber length after baking

[0045] The fiber length retention is more preferably 95 % or more. The reason why the tensile elongation of the pitch-based carbon fiber becomes higher than before when the fiber length retention is higher than 90 % is not known yet. It is known that the carbonization of mesophase pitch goes through a liquid phase. In the process of the present invention, the stabilized fibers must be prepared by adding more highly concentrated oxygen than before to the carbon fiber precursors. Therefore, it is assumed that the oxygen crosslinking of the carbon fiber precursors proceeds, thereby changing liquid-phase carbonization to solid-phase carbonization.

[short fibers]

[0046] To obtain pitch-based carbon fibers having a desired fiber length, the obtained nonwoven fabric may be cut and milled/ground. Or, it may be classified according to the circumstances. Processing system is selected according to a desired fiber length. A guillotine cutter, or a single-screw, double-screw or multi-screw rotary cutter is preferably used for cutting. For milling and grinding, a hammer, pin, ball, bead or rod type milling or grinding machine which makes use of impact action, a high-speed rotary milling or grinding machine which makes use of an impact between particles, and a roll, cone or screw type milling or grinding machine which makes use of compression or tear action are preferably used.

[0047] To obtain a desired fiber length, cutting and milling/grinding may be carried out with different types of machines and the processing atmosphere may be wet or dry. A vibration sieve type, centrifugal type, inertia force type or filtration type classifier is preferably used for classification. A desired fiber length can be obtained not only by selecting the type of a machine but also by controlling the revolution of a rotor or rotary blade, the amount of supply, clearance between blades and residence time in system. When classification is carried out, a desired fiber length can also be obtained by controlling the opening diameter of a sieve net. Pitch-based carbon short fibers can be obtained by these processings.

[0048] The nonwoven fabric containing pitch-based carbon fibers obtained as described above or the pitch-based carbon short fibers obtained by milling may be further heated at 2,000 to 3, 500°C to be graphitized so as to obtain the final nonwoven fabric containing pitch-based graphitized fibers or pitch-based graphitized short fibers. Graphitization is carried out in an Acheson furnace or electric furnace in vacuum or a non-oxidative atmosphere using an inert gas such as nitrogen, argon or krypton.

[felt]

[0049] Since the nonwoven fabric of the present invention is composed of pitch-based carbon fibers having a high elongation and a high elastic modulus, it is suitable for needle punching and a felt can be advantageously obtained from the nonwoven fabric of the present invention. The present invention includes a felt obtained by needle punching the above nonwoven fabric.

[0050] The delamination strength in the thickness direction of the felt of the present invention is preferably 0.25 N/5 cm piece or more, more preferably 0.35 N/5 cm piece. When the delamination strength is lower than 0.25 N/5 cm piece, interlacing between crosslapped layers becomes unsatisfactory, thereby causing delamination at the time of processing, deteriorating handling ease, and causing nonuniformity in physical properties. The term "delamination strength" means interlacing strength in the thickness direction of a felt. This is obtained from maximum strength when the felt is cut with a cutting knife in a direction parallel to the layer direction at an intermediate position in the thickness direction of the felt and both ends are pulled with a tensile tester at a rate of 100 mm/min.

[0051] The carbon fibers constituting the felt of the present invention preferably have an average fiber diameter measured by an optical microscope of more than 2 μm and 20 μm or less. When the average fiber diameter is 2 μm or less, a void portion is made fine, whereby resin impregnation at the time of molding may become unsatisfactory. When the average fiber diameter is larger than 20 μm, the void portion becomes huge, whereby heat conductivity at a high-temperature range in which the domination of radiation heat is strong becomes high, thereby reducing heat insulating properties. The average fiber diameter is more preferably more than 10 μm and 20 μm or less, much more preferably more than 10 μm and 15 μm or less from the viewpoint of improving oxidation resistance and strength.

[0052] The weight of the felt of the present invention is preferably 250 to 1,000 g/m^2. The weight can be adjusted according to application purpose but optimally 250 to 1,000 g/m^2 for the continuous stable production of the felt. When the weight is lower than 250 g/m^2, as the pitch-based carbon fiber web is thin, the web may be broken or creased by felting. When the weight is higher than 1,000 g/m^2, as the thickness is large, the heat of the pitch-based stabilized fiber web is not smoothly removed at the time of stabilization, whereby fusion between fibers may occur. The weight is more preferably 400 to 700 g/m^2.

[0053] Therefore, it is preferred that the felt of the present invention should have an average fiber diameter of carbon fibers of more than 10 μm and 20 μm or less and a weight of 250 to 1,000 g/m^2. The present invention includes a graphitized felt obtained by further heating the above felt at 2,000 to 3,500°C.

[0054] It is preferred that the graphitized felt of the present invention should have an average fiber diameter of graphitized fibers of more than 2 μm and 20 μm or less and a weight of 250 to 1,000 g/m^2. Since the graphitized felt is produced from the above felt, its weight is lower than the weight of its parent felt by a weight lost by graphitization. The weight of the graphitized felt can be suitably adjusted by selecting the weight of its parent felt.

[0055] When the weight of the parent felt is lower than 250 g/m^2, as the pitch-based carbon fiber web is thin, the web may be broken or creased by felting. When the weight is higher than 1,000 g/m^2, as the thickness is large, the heat of the pitch-based stabilized fiber web cannot be removed smoothly at the time of stabilization, whereby fusion between fibers may occur. The weight is more preferably 400 to 700 g/m^2.

[0056] Preferably, the graphitized felt of the present invention has a weight loss of less than 10 wt% of its initial weight when it is heated at a temperature elevation rate of 3°C/min in the air. When the weight loss is 10 wt% or more of the initial weight, oxidation resistance greatly degrades and characteristic properties required when used as a heat insulating material cannot be obtained fully disadvantageously. The weight loss when heated at a temperature elevation rate of 3°C/min in the air is preferably 8 wt% or less, more preferably 5 wt% or less. The weight loss when heated at a temperature elevation rate of 3°C/min in the air can be measured, for example, with a differential thermogravimetric analyzer.

[0057] The graphitized felt of the present invention has a lower degree of graphitization than a graphitized felt produced from the felt of the prior art. Therefore, it has low heat conductivity and shows excellent heat insulating characteristics when it is used as a heat insulating material. Although the reason why the degree of graphitization of the graphitized felt of the present invention is low is not known yet, since more highly concentrated oxygen than before must be added to the carbon fiber precursors so as to produce stabilized fibers in the process of the present invention, it is assumed that the oxygen crosslinking of the carbon fiber precursors proceeds, thereby changing liquid-phase carbonization to solid-phase carbonization.

[production process of felt]

[0058] The present invention includes a process for producing a felt, comprising the steps of:

(1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors [step (1)];
(2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including stabilized fibers containing 8 to 15 wt% of oxygen [step (2)];
(3) baking the stabilized web at 800 to 1,800°C to produce a nonwoven fabric [step (3)] ; and
(4) needle punching the nonwoven fabric [step (4)].

[0059] The steps (1) to (3) are the same as in the above-described production process of the nonwoven fabric. The conveyance speed ratio in the step (2) and the step (3) is preferably optimized against heat shrinkage. Since it has been known that pitch-based carbon fibers spun by the melt blowing method are collected and crosslapped to improve productivity, it has been difficult to carry out the interlacing of crosslapped layers. This is because a single-layer web to be crosslapped is strongly interlaced when it is collected after spinning, whereby even when felting such as needle punching is carried out on a laminate, carbon fibers hardly move in the thickness direction. Further, as the carbon fibers are hard and fragile, the fibers are broken simply by increasing the number of punches, thereby reducing strength and yield. Therefore, to interlace the fibers without increasing the number of punches, the shape of the needle is preferably optimized.

[0060] Since heat shrinkage occurs when the stabilized web is baked to produce a nonwoven fabric, when the continuous process is employed, the stabilized web is pulled at the time of baking and therefore, the carbon fibers are strained in the web. Further, the web is often torn. When the carbon fibers are strained in the web, it is difficult to carry out felting such as needle punching, which causes the breakage of fibers and reduces delamination strength. Therefore, means for the alleviation of heat shrinkage at the time of baking is required and therefore, the ratio of the conveyance speed in the step (2) (stabilization) to the conveyance speed in the step (3) (baking) is preferably optimized against heat shrinkage. That is, the V1/V2 ratio of the conveyance speed V1 of the web in the step (2) to the conveyance speed V2 of the web in the step (3) is preferably 1.01 to 1.10.

[0061] The step (4) is to needle punch the nonwoven fabric. The number of punches for needle punching is preferably 1 to 200/cm^2, more preferably 15 to 100/cm^2. The depth of the barb of the needle is preferably 0.15 mm or more, more preferably 0.2 to 0.4 mm. Therefore, in the step (4), the nonwoven fabric is preferably punched 15 to 100 times/cm^2 with a needle having a barb depth of 0.15 mm or more.

[0062] When the depth of the barb is smaller than 0.15 mm, interlacing is insufficient with 15 to 100 punches/cm^2, and satisfactory delamination strength is not obtained. When the number of punches is 15 or less/cm^2, even if the depth of the barb is 0.15 mm or more, interlacing is insufficient and satisfactory delamination strength is not obtained. When the number of punches is 100 or more/cm^2, the breakage of fibers often occurs, thereby reducing strength and yield. The depth of the barb is more preferably 0.20 mm or more and the number of punches is more preferably 15 to 50/cm^2.

[0063] The depth of the barb is the depth of a cut called "barb" in the needle as shown in Fig. 1. The barb portion has a projection called "kick-up".

[0064] The height of the kick-up, the number of barbs, the interval between adjacent barbs and the depth of the needle are suitably selected according to the weight and thickness of the nonwoven fabric to be felted. The height of the kick-up is selected from a range from 0 to 0.15 mm. When the height of the kick-up is larger than 0.15 mm, the breakage of fibers often occurs, thereby reducing strength and yield. The number of barbs may be suitably selected from a range from 3 to 18. When the number of barbs is smaller than 3, interlacing is insufficient and satisfactory delamination strength may not be obtained. When the number of barbs is larger than 18, the breakage of fibers often occurs, whereby strength and yield may lower. The interval between adjacent barbs is suitably selected from a range from 0.3 to 3 mm. The term "interval between adjacent barbs" in the present invention includes an interval between adjacent barbs of different rows of a blade. When the interval between adjacent barbs is smaller than 0.3 mm, the breakage of fibers often occurs, whereby strength and yield may lower. When the interval is larger than 3 mm, interlacing is insufficient and satisfactory delamination strength may not be obtained. The depth of the needle is suitably selected from a range from 0 to 20 mm. The depth of the needle indicates how deep the needle is stuck into the felt and is represented by the distance between a bed plate and a barb (commonly called "first barb") at the shortest distance from the distal end of the needle at the time of needle punching. When the depth of the needle is smaller than 0 mm, interlacing is insufficient and satisfactory delamination strength may not be obtained. When the depth of the needle is larger than 20 mm, the breakage of fibers often occurs, whereby strength and yield may lower.

[0065] Fig. 1 and Fig. 2 schematically show the height of the kick-up, the depth of the needle and the interval between adjacent barbs.

[0066] Since the carbon fibers constituting the nonwoven fabric of the present invention have a high elongation and a high elastic modulus, they are suitable for needle punching. The bulk density of the felt is set to preferably 0.01 to 0.5 g/cm^3, more preferably 0.03 to 0.3 g/cm^3 by needle punching. The thickness of the felt may be selected according to application purpose and not particularly limited but generally 1 to 100 mm, preferably 5 to 50 mm. The felt of the present invention can be advantageously used in heat insulating materials and acoustic insulating materials.

[composite]

[0067] The present invention includes a composite obtained by impregnating the above felt with a resin. The resin is preferably a thermosetting resin. The composite can be obtained by impregnating the felt with a thermosetting resin, pressure molding and thermally curing it.

[0068] Examples of the thermosetting resin include phenol resin, epoxies, acrylics, urethanes, silicones, imides, thermosetting modified PPE's, thermosetting PPE's, polybutadiene-based rubber and copolymers thereof, acrylic rubber and copolymers thereof, silicone-based rubber and copolymers thereof, and natural rubber. They may be used alone or in combination of two or more. The amount of the resin is preferably 50 to 1,000 parts by weight, more preferably 100 to 700 parts by weight based on 100 parts by weight of the felt. The above graphitized felt may be used as the above felt.

[heat insulating material]

[0069] The present invention includes a heat insulating material obtained by heating the above composite at 500 to 2,200°C. That is, the heat insulating material of the present invention can be manufactured by (1) impregnating the above felt with a resin to produce a composite and (2) heating, that is, carbonizing the above composite at 500 to 2,200°C. The temperature of heating, that is, carbonization is preferably 800 to 2,000°C.

[0070] The average fiber diameter of the carbon fibers constituting the heat insulating material should be more than 2 μm and 20 μm or less. When the average fiber diameter is more than 10 μm and 20 μm or less, preferably more than 10 μm and 15 μm or less, the obtained heat insulating material becomes excellent in oxidation resistance and strength, hardly deteriorates by oxidation even at a high temperature, has excellent durability and is preferably used as a heat insulating material for high-temperature processing furnaces.

[0071] The heat insulating material contains a carbide in an amount of 50 to 1,000 parts by weight based on 100 parts by weight of the pitch-based carbon fiber felt. The term "carbide" as used herein means a component which is obtained by carbonizing a thermosetting resin when the above composite is heated. When the amount of the carbide is smaller than 50 parts by weight, the number of voids in the felt is small, that is, the bulk density of the felt is high, thereby reducing heat insulating properties. When the amount of the carbide is larger than 1,000 parts by weight, the obtained heat insulating material is essentially composed of a carbide derived from a thermosetting resin and the amount of a felt which can be expected to be resistant to oxidation becomes small disadvantageously. The amount of the carbide is preferably 100 to 700 parts by weight based on 100 parts by weight of the felt. The weight ratio of the carbide to the felt can be calculated from the weight of the carbide obtained by subtracting the weight of the pitch-based carbon fiber felt measured in advance from the weight of the obtained composite.

[0072] Generally speaking, since a heat insulating material is used under a severe condition such as a high temperature, high durability is required. The felt comprising the pitch-based carbon fibers of the present invention is hardly deteriorated by oxidation even at a high temperature, and the composite is also hardly deteriorated by oxidation. Therefore, as the heat insulating material of the present invention has excellent durability, it can be used in a high-temperature processing furnace.

Examples

[0073] The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

[0074] Physical properties were measured by the following methods in Examples 1 to 13 and Comparative Examples 1 to 5.

(1) Average fiber diameter (D1) and degree of fiber diameter distribution (S1) of carbon fibers

[0075] The average fiber diameter (D1) was obtained from an average value of 60 carbon fibers measured by using a scale under an optical microscope. The CV value was determined from the following equation as a percentage of the degree of fiber diameter distribution (S1) to the obtained average fiber diameter (D1).

$$CV = S1/D1 \times 100$$

wherein

$$S1 = \sqrt{((\Sigma X - D1)^2 / n)} ,$$

X is an observation value, and n is the number of observations.

(2) Average fiber length of carbon fiber precursors

[0076] The average fiber length of carbon fiber precursors is obtained by collecting a bundle of carbon fiber precursors with three fiber collection brushes installed at a position 30 cm below the spinneret, measuring the lengths of these bundles and averaging the measurement values.

(3) Fiber length retention

[0077] The fiber length retention was obtained from the values of the fiber length (L^1) of a carbon fiber baked at 800°C and of the fiber length (L^0) before baking based on the following equation (I).

$$\text{Fiber length retention} = 100 \times L^1/L^0 \qquad (I)$$

L^0: fiber length before baking
L^1: fiber length after baking

[0078] The fiber length (L^1) of the carbon fiber was obtained by extracting 10 carbon fibers from a nonwoven fabric baked at 800°C, measuring their lengths and averaging the measurement values. The fiber length (L^0) before baking was obtained by extracting 10 carbon fibers from the stabilized web, measuring their lengths and averaging the measurement values.

(4) Amount of oxygen added to stabilized fiber

[0079] The amount of oxygen added to a stabilized fiber was measured with CHNS-O Analyzer (FLASH EA 1112 Series of Thermoelectron Corporation).

(5) Tensile elongation and tensile elastic modulus of carbon fiber and tensile strength of nonwoven fabric

[0080] The tensile elongation and tensile elastic modulus of carbon fibers were determined by stretching yarn composed of 120 carbon fibers, measuring the fiber diameter of each of the carbon fibers, measuring the mechanical strengths of the 120 carbon fibers with a Tensilon measurement instrument (ORIENTEC RTC-1150A) and obtaining the number average values of tensile elongation and tensile elastic modulus.

(6) Tensile strength of nonwoven fabric

[0081] Samples having a width of 5 cm and a length of 20 cm were extracted from 6 portions which consisted of 2 left portions, 2 middle portions and 2 right portions in the crosswise direction of a nonwoven fabric and pulled in the lengthwise direction with a tensile tester at a rate of 100 mm/min, and the average value of the strengths of these samples was calculated to determine the tensile strength of the nonwoven fabric.

(7) Delamination strength of felt

[0082] Samples having a width of 5 cm and a length of 20 cm were extracted from 6 portions which consisted of 2 left portions, 2 middle portions and 2 right portions in the crosswise direction of a felt and cut in a direction parallel to the layer direction at an intermediate position in the thickness direction of each sample, both ends of these samples were pulled with a tensile tester at a rate of 100 mm/min, and the average value of the maximum strengths of these samples was calculated to obtain the delamination strength of the felt.

(8) Weight of felt

[0083] A4-sized samples were cut away from 6 portions which consisted of 2 left portions, 2 middle portions and 2 right portions in the crosswise direction of a felt to measure their weights so as to calculate the weight of the felt.

(9) Tensile strength of heat insulating material

[0084] The tensile strength of a heat insulating material was measured with a large-size characteristic tester (SS-207-5P of Toyo Baldwin Co. Ltd.).

(10) Section of composite of phenol-based resin

[0085] The section of a composite was observed through a scanning electron microscope at a magnification of 1,000X to confirm a void in the composite.

(11) Heat conductivity of heat insulating material

[0086] This was obtained by a probe method using the QTM-500 of Kyoto Electron Co., Ltd.

(12) Weight ratio of carbide to carbon fiber felt

[0087] The weight of a carbide was obtained by subtracting the weight of a carbon fiber felt measured in advance from the weight of the obtained composite.

(13) Oxidation resistance of graphitized felt

[0088] The weight loss of a graphitized felt at 700°C was measured with a differential thermogravimetric analyzer (TG8120 of Rigaku Denki Co. , Ltd.) by raising the temperature from room temperature at a rate of 3°C/min in the air.

Example 1

(spinning)

[0089] Molten mesophase pitch composed of an aromatic hydrocarbon and having a mesophase content of 100 % and a softening temperature of 278°C was drawn at 335°C by blowing 339°C air from a slit beside the capillaries at a rate of 8,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web containing carbon fibers having an average diameter of 13 .0 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 8.4 cm.

(stabilization)

[0090] Then, the precursor web was heated from 200 to 340°C in an air atmosphere in 30 minutes to produce a stabilized web composed of stabilized fibers. The amount of oxygen added to the stabilized fibers was 10.9 wt%. The average fiber length of the stabilized fibers was 8.5 cm.

(baking)

[0091] Then, the stabilized web was baked at 800°C in a nitrogen atmosphere continuously to produce a nonwoven fabric composed of carbon fibers. At this point, the V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was 1.03. The average fiber diameter of the obtained carbon fibers was 12.1 μm, and the CV value of the fiber diameter was 10.2 %. The average fiber length of the carbon fibers was 8.1 cm, and the fiber length retention was 95 %. When the tensile strength of a nonwoven fabric composed of the carbon fibers was measured, it was 15.5 N/5 cm piece.

[0092] The stabilized web was baked at 1,500°C from room temperature in an argon gas atmosphere over 1 hour to obtain a nonwoven fabric composed of the carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 1.61 %, the tensile strength was 3.0 GPa, and the tensile elastic modulus was 240 GPa.

Example 2 (felt)

[0093] The nonwoven fabric composed of carbon fibers obtained in Example 1 was punched 20 times/cm^2 with a needle having a kick-up height of 0.05 mm, 9 barbs, an interval between adjacent barbs of 3 mm and a barb depth of 0.25 mm at a needle depth of 10 mm to obtain a felt. The obtained felt had a delamination strength of 0.45 N/5 cm piece, an average fiber diameter of 12.1 μm and a weight of 445 g/m^2.

Example 3 (composite - heat insulating material)

[0094] The felt produced in Example 2 was immersed in a phenol resin (PL-2211 of Gunei Kagaku Co., Ltd., viscosity of 0.1 Pa·s), compressed with a roll press to squeeze out excess phenol resin and molded at 250°C to produce a composite which was then baked at 800°C. The composite was further heat-treated at 2,000°C to obtain a carbon fiber-containing heat insulating material. A carbide was contained in an amount of 400 parts by weight based on 100 parts by weight of the carbon fiber felt. When the section of the baked product was observed, no void was seen. The tensile strength of the heat insulating material was 0.74 MPa, and the heat conductivity was 0.048 W/m·K. After the heat insulating material was treated at 2,000°C and an oxygen concentration of 20 ppm for 24 hours, its tensile strength was 0.68 MPa.

Example 4 (graphitized felt)

[0095] The felt produced in Example 2 was baked at 2,000°C from room temperature in an argon gas atmosphere over 3 hours to obtain a graphitized felt. The weight of the graphitized felt was 438 g/m^2, and the average fiber diameter of single yarn constituting the graphitized felt was 11.3 μm. The weight loss at 700°C of the graphite felt when it was heated from room temperature up to 700°C in the air at a rate of 3°C/min was 4.8 wt% of its initial weight.

Example 5 (graphitized felt - heat insulating material)

[0096] The graphitized felt produced in Example 4 was immersed in a phenol resin (PL-2211 of Gunei Kagaku Co., Ltd., viscosity of 0.1 Pa·s), compressed with a roll press to squeeze out excess phenol resin and molded at 250°C to produce a composite which was then baked at 800°C. Further, the composite was heat-treated at 2, 000°C to obtain a graphitized fiber-containing heat insulating material. A carbide was contained in an amount of 405 parts by weight based on 100 parts by weight of the graphitized fiber felt. When the section of the baked product was observed, no void was seen. The tensile strength of the heat insulating material was 1.23 MPa, and the heat conductivity was 0.078 W/m·K. After the heat insulating material was treated at 2, 000°C and an oxygen concentration of 20 ppm for 24 hours, its tensile strength was 1.18 MPa.

Example 6

(spinning)

[0097] Molten mesophase pitch composed of an aromatic hydrocarbon and having a mesophase content of 100 % and a softening temperature of 278°C was drawn at 331°C by blowing 336°C air from a slit beside capillaries at a rate of 8,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web having an average diameter of 11.0 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 15.3 cm.

(stabilization)

[0098] Then, the precursor web was heated from 200 to 340°C in an air atmosphere in 30 minutes to produce a stabilized web composed of stabilized fibers. The amount of oxygen added to the stabilized fibers was 11.8 wt%. The average fiber length of the stabilized fibers was 15.2 cm.

(baking)

[0099] Then, the stabilized web was baked at 800°C in a nitrogen atmosphere continuously to produce a nonwoven fabric composed of carbon fibers. At this point, the V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was 1.02. The average fiber diameter of the obtained carbon fibers was 10.3 μm, and the CV value of the fiber diameter was 8.2 %. The average fiber length of the carbon fibers was 14.2 cm, and the fiber length retention was 93 %. When the tensile strength of the nonwoven fabric composed of the carbon fibers was measured, it was 14.6 N/5 cm piece.

[0100] The obtained stabilized web was baked at 1, 500°C from room temperature in an argon gas atmosphere over 1 hour to obtain a nonwoven fabric composed of the carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 1.55 %, the tensile strength was 3.1 GPa, and the tensile elastic modulus was 235 GPa.

Example 7 (felt)

[0101] The nonwoven fabric composed of carbon fibers obtained in Example 6 was punched 25 times/cm^2 with a needle having a kick-up height of 0.04 mm, 9 barbs, an interval between adjacent barbs of 3 mm and a barb depth of 0.20 mm at a needle depth of 10 mm to obtain a felt. The obtained felt had a delamination strength of 0.48 N/5 cm piece, an average fiber diameter of 10.5 μm and a weight of 390 g/m^2.

Example 8 (composite - heat insulating material)

[0102] The felt produced in Example 7 was immersed in a phenol resin (PL-2211 of Gunei Kagaku Co., Ltd., viscosity of 0.1 Pa·s), compressed with a roll press to squeeze out excess phenol resin and molded at 250°C to produce a composite which was then baked at 800°C. Further, the composite was baked at 2,000°C to obtain a carbon fiber-containing heat insulating material. A carbide was contained in an amount of 400 parts by weight based on 100 parts by weight of the felt. When the section of the baked product was observed, no void was seen. The tensile strength of the heat insulating material was 0.79 MPa, and the heat conductivity was 0.049 W/m·K. After the heat insulating material was treated at 2, 000°C and an oxygen concentration of 20 ppm for 24 hours, its tensile strength was 0.76 MPa.

Example 9 (graphitized felt)

[0103] The felt produced in Example 7 was baked at 2,500°C from room temperature in an argon gas atmosphere over 3 hours to obtain a graphitized felt. The weight of the graphitized felt was 385 g/m^2, and the average fiber diameter of single yarn constituting the graphitized felt was 9.8 μm. The weight loss at 700 °C of the graphitized felt when it was heated from room temperature up to 700°C in the air at a rate of 3°C/min was 3.8 wt% of its initial weight.

Example 10

(spinning)

[0104] Molten mesophase pitch composed of an aromatic hydrocarbon and having a mesophase content of 100 %

and a softening temperature of 278°C was drawn at 336°C by blowing 339°C air from a slit beside capillaries at a rate of 5,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web composed of carbon fiber precursors having an average diameter of 15. 1 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 10.4 cm.

(stabilization)

[0105] Then, the precursor web was heated from 200 to 340°C in an air atmosphere in 30 minutes to produce a stabilized web composed of stabilized fibers. The amount of oxygen added to the stabilized fibers was 8.4 wt%. The average fiber length of the stabilized fibers was 10.4 cm.

(baking)

[0106] Then, the stabilized web was baked at 800°C in a nitrogen atmosphere continuously to produce a nonwoven fabric composed of the carbon fibers. At this point, the V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was 1.04. The average fiber diameter of the carbon fibers was 14.3 μm, and the CV value of the fiber diameter was 10. 5 %. The average fiber length of the carbon fibers was 9.5 cm, and the fiber length retention was 91 %. When the tensile strength of the nonwoven fabric composed of the carbon fibers was measured, it was 15.6 N/5 cm piece. The nonwoven fabric composed of the stabilized fibers was baked at 1,500°C from room temperature in an argon gas atmosphere over 1 hour to obtain a nonwoven fabric composed of carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 1.48 %, the tensile strength was 2.6 GPa, and the tensile elastic modulus was 253 GPa.

Example 11 (felt)

[0107] The nonwoven fabric composed of carbon fibers obtained in Example 10 was punched 30 times/cm^2 with a needle having a kick-up height of 0.05 mm, 9 barbs, an interval between adjacent barbs of 3 mm and a barb depth of 0.30 mm at a needle depth of 10 mm to obtain a felt. The obtained felt had a delamination strength of 0.39 N/5 cm piece, an average fiber diameter of 14.3 μm and a weight of 460 g/m^2.

Example 12 (composite - heat insulating material)

[0108] The felt produced in Example 11 was immersed in a phenol resin (PL-4222 of Gunei Kagaku Co., Ltd., viscosity of 0.5 Pa·s), compressed with a roll press to squeeze out excess phenol resin and molded at 250°C to produce a composite which was then baked at 800°C. Further, the composite was baked at 2,000°C to obtain a carbon fiber-containing heat insulating material. A carbide was contained in an amount of 400 parts by weight based on 100 parts by weight of the carbon fiber felt. When the section of the baked product was observed, no void was seen. The tensile strength of the heat insulating material was 0.83 MPa, and the heat conductivity was 0.049 W/m·K. After the heat insulating material was treated at 2, 000°C and an oxygen concentration of 20 ppm for 24 hours, its tensile strength was 0.78 MPa.

Example 13 (graphitized felt)

[0109] The felt produced in Example 11 was baked at 3, 000°C from room temperature in an argon gas atmosphere over 3 hours to obtain a graphitized felt. The weight of the graphitized felt was 452 g/m^2, and the average fiber diameter of single yarn constituting the graphitized felt was 13.8 μm. The weight loss at 700°C of the graphitized felt when it was heated from room temperature up to 700°C in the air at a rate of 3°C/min was 3.1 wt% of its initial weight.

Comparative Example 1

(spinning)

[0110] Molten mesophase pitch composed of an aromatic hydrocarbon and having a mesophase content of 100 % and a softening temperature of 278°C was drawn at 335°C by blowing 339°C air from a slit beside capillaries at a rate of 8,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web composed of carbon fiber precursors having an average diameter of 13.0 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 8.4 cm.

(stabilization)

[0111] Then, the precursor web was heated from 200 to 290°C in an air atmosphere in 30 minutes to produce a stabilized web composed of stabilized carbon fibers. The amount of oxygen added to the stabilized carbon fibers was 6.5 wt%. The average fiber length of the stabilized fibers was 8.5 cm.

(baking)

[0112] The V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was set to 1.00, and an attempt was made to obtain a nonwoven fabric composed of carbon fibers by baking at 800°C in a nitrogen atmosphere continuously. However, a break in a nonwoven fabric composed of carbon fibers due to the shrinkage of the web was observed. The average fiber diameter of the carbon fibers was 12.1 μm, and the CV value of the fiber diameter was 10.2 %. The average fiber length of the pitch-based carbon fibers was 7.3 cm, and the fiber length retention was 86 %. When the tensile strength of a nonwoven fabric composed of the pitch-based carbon fibers was measured, it was 6.7 N/5 cm piece.

[0113] The obtained stabilized web was baked at 1, 500°C from room temperature in an argon gas atmosphere over 1 hour to obtain a nonwoven fabric composed of the pitch-based carbon fibers. When the mechanical properties of the pitch-based carbon fibers were evaluated, the tensile elongation was 1.2 %, the tensile strength was 1.7 GPa, and the tensile elastic modulus was 216 GPa.

Comparative Example 2 (felt)

[0114] The nonwoven fabric composed of carbon fibers obtained in Comparative Example 1 was punched 20 times/cm^2 with a needle having a kick-up height of 0.05 mm, 9 barbs, an interval between adjacent barbs of 3 mm and a barb depth of 0.25 mm at a needle depth of 10 mm to obtain a felt. The obtained felt had a delamination strength of 0.15 N/5 cm piece, an average fiber diameter of 12.1 μm and a weight of 218 g/m^2. To produce a heat insulating material, an attempt was made to immerse the obtained felt in a phenol resin (PL-4222 of Gunei Kagaku Co., Ltd., viscosity of 0.5 Pa·s) but the felt was broken due to its insufficient strength.

Comparative Example 3

(spinning)

[0115] Molten mesophase pitch composed of an aromatic hydrocarbon and having a mesophase content of 100 % and a softening temperature of 278°C was drawn at 328°C by blowing 335°C air from a slit beside capillaries at a rate of 3,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web composed of carbon fiber precursors having an average diameter of 21.5 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 30.4 cm.

(stabilization)

[0116] Then, the precursor web was heated from 200°C to 340°C in an air atmosphere in 30 minutes to produce a stabilized web composed of stabilized carbon fibers. The amount of oxygen added to the stabilized carbon fibers was 6.6 wt%. The average fiber length of the pitch-based stabilized fibers was 30.5 cm.

(baking)

[0117] The V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was set to 1.00, and an attempt was made to obtain a nonwoven fabric composed of carbon fibers by baking at 800°C in a nitrogen atmosphere continuously. However, a break in a nonwoven fabric composed of carbon fibers due to the shrinkage of the web was observed. The average fiber diameter of the carbon fibers was 20.5 μm, and the CV value of the fiber diameter was 9.2 %. The average fiber length of the carbon fibers was 25.9 cm, and the fiber length retention was 85 %. When the tensile strength of the nonwoven fabric composed of the carbon fibers was measured, it was 8.4 N/5 cm piece.

[0118] The obtained stabilized web was baked at 1, 500°C from room temperature in an argon gas atmosphere over

1 hour to obtain a nonwoven fabric composed of the carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 1.3 %, the tensile strength was 1.6 GPa, and the tensile elastic modulus was 235 GPa.

Comparative Example 4

(spinning)

[0119] Molten isotropic pitch composed of an aromatic hydrocarbon and having a mesophase content of 0 % and a softening temperature of 258°C was drawn at 295°C by blowing 305°C air from a slit beside capillaries at a rate of 5,000 m/min using a spinneret having capillaries with a diameter of 0.2 mm and a length of 2 mm so as to produce a precursor web composed of carbon fiber precursors having an average diameter of 13.5 μm. When the carbon fiber precursors right below the spinneret were collected with a wire brush to measure the average fiber length of the carbon fiber precursors, it was 17.4 cm.

(stabilization)

[0120] Then, the precursor web was heated from 200°C to 320°C in an air atmosphere in 40 minutes to produce a stabilized web composed of stabilized carbon fibers. The amount of oxygen added to the stabilized carbon fibers was 8.6 wt%. The average fiber length of the stabilized fibers was 17.5 cm.

(baking)

[0121] Then, a nonwoven fabric composed of carbon fibers was produced continuously by baking the stabilized web at 800°C in a nitrogen atmosphere. At this point, the V1/V2 ratio of the conveyance speed V1 of the web at the time of stabilization to the conveyance speed V2 of the web at the time of baking was 1.00. The average fiber diameter of the carbon fibers was 12.5 μm, and the CV value of the fiber diameter was 11.2 %. The average fiber length of the carbon fibers was 16.9 cm, and the fiber length retention was 96.6 %. When the tensile strength of the nonwoven fabric composed of the carbon fibers was measured, it was 9.5 N/5 cm piece.

[0122] The obtained stabilized web was baked at 1, 500°C from room temperature in an argon gas atmosphere over 1 hour to obtain a nonwoven fabric composed of the carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 2.2 %, the tensile strength was 0.7 GPa, and the tensile elastic modulus was 29 GPa.

Comparative Example 5

[0123] The stabilized web composed of stabilized carbon fibers produced in Example 1 was baked at 2,300°C from room temperature in an argon gas atmosphere over 2 hours to obtain a nonwoven fabric composed of carbon fibers. When the mechanical properties of the carbon fibers were evaluated, the tensile elongation was 0.63 %, the tensile strength was 2.4 GPa, and the tensile elastic modulus was 510 GPa.

Effect of the Invention

[0124] Since the nonwoven fabric of the present invention contains carbon fibers having a high elongation and a high elastic modulus, it has excellent mechanical strength and is suitable for needle punching and felting. According to the process for producing a nonwoven fabric of the present invention, by setting the amount of oxygen added to the stabilized fibers to a specific range, the tensile elongation of pitch-based carbon fibers can be enhanced. The felt of the present invention is excellent in mechanical strength, especially delamination strength. According to the process for producing a felt of the present invention, a felt which is excellent in mechanical strength, especially delamination strength, can be obtained. The heat insulating material of the present invention has excellent mechanical strength and heat insulating properties.

Industrial Applicability

[0125] The nonwoven fabric, felt and heat insulating material of the present invention can be used in structural members for industrial robot arms and airplanes.

Claims

1. A nonwoven fabric containing pitch-based carbon fibers, wherein the pitch-based carbon fibers have (i) an average fiber diameter (D1) measured by an optical microscope of more than 2 μm and 20 μm or less, (ii) a percentage of the degree of fiber diameter distribution (S1) to average fiber diameter (D1) measured by an optical microscope of 3 to 20 %, (iii) a tensile elastic modulus of 80 to 300 GPa and (iv) a tensile elongation of 1.4 to 2.5 %.

2. The nonwoven fabric according to claim 1, wherein the pitch-based carbon fibers have a tensile elastic modulus of 100 to 300 GPa and a tensile elongation of 1.5 to 2.4 %.

3. The nonwoven fabric according to claim 1, wherein the average fiber diameter (D1) measured by an optical microscope of the pitch-based carbon fibers is more than 10 μm and 20 μm or less.

4. The nonwoven fabric according to claim 1 which has a tensile strength of 10 N/5 cm piece or more.

5. A process for producing a nonwoven fabric, comprising the steps of:

   (1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors;
   (2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including carbon fibers containing 8 to 15 wt% of oxygen; and
   (3) baking the stabilized web at 800 to 1,800°C.

6. The production process according to claim 5, wherein spinning is carried out by a melt blowing method.

7. The production process according to claim 5, wherein the average fiber length of the carbon fiber precursors of the precursor web is 4 to 25 cm.

8. The production process according to claim 5, wherein the amount of oxygen added to the carbon fibers of the stabilized web is 9 to 12 wt%.

9. The production process according to claim 5, wherein the fiber length retention (%) defined by the following equation (I) before and after baking is 90 % or more.

$$\text{Fiber length retention} = 100 \times L^1/L^0 \qquad (I)$$

   L^0: fiber length before baking
   L^1: fiber length after baking

10. A felt obtained by needle punching the nonwoven fabric of claim 1.

11. The felt according to claim 10 which has a delamination strength in the thickness direction of 0.25 N/5 cm piece or more.

12. The felt according to claim 10, wherein the carbon fibers have an average fiber diameter of more than 10 μm and 20 μm or less and a weight of 250 to 1,000 g/m^2.

13. A graphitized felt obtained by further heating the felt of claim 10 at 2,000 to 3,500°C.

14. A process for producing a felt, comprising the steps of:

   (1) spinning mesophase pitch to produce a precursor web containing carbon fiber precursors;
   (2) stabilizing the precursor web in an oxidative gas atmosphere to produce a stabilized web including carbon fibers containing 8 to 15 wt% of oxygen;
   (3) baking the stabilized web at 800 to 1,800°C to produce a nonwoven fabric; and
   (4) needle punching the nonwoven fabric.

15. The production process according to claim 14, wherein the nonwoven fabric is punched 15 to 100 times/cm^2 with a needle having a barb depth of 0.15 mm or more.

16. A composite obtained by impregnating the felt of claim 10 with a resin.

17. A composite obtained by impregnating the graphitized felt of claim 13 with a resin.

18. A heat insulating material obtained by heating the composite of claim 16 at 500 to 2,200°C.

19. A process for producing a heat insulating material, comprising the steps of:

(1) impregnating the felt of claim 10 with a resin to produce a composite; and
(2) heating the composite at 500 to 2,200°C.

Fig. 1

a schematic diagram of the barb portion of a needle

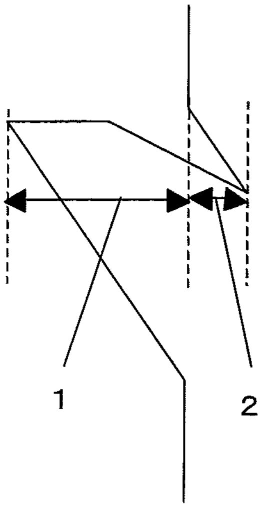
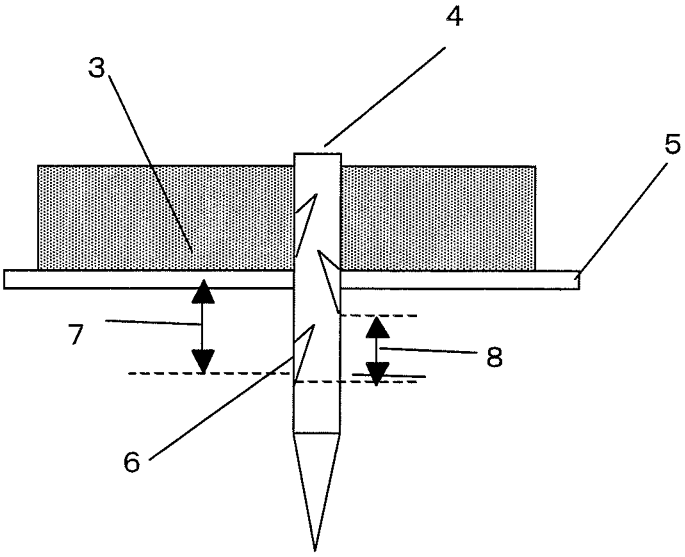


Fig. 2

a schematic diagram of the needle



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/054008

A. CLASSIFICATION OF SUBJECT MATTER
D01F9/145(2006.01)i, *D04H1/42*(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)
D01F9/08-9/32, D04H1/00-18/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 5-195396 A (Petoca, Ltd.), 03 August, 1993 (03.08.93), Par. Nos. [0001], [0007], [0008], [0015], [0018], [0027] & EP 543147 A1 Column 1, lines 1 to 19; column 3, line 46 to column 4, line 32; column 6, lines 21 to 47; column 7, lines 26 to 44; column 10, line 30 to column 11, line 19 & US 5283113 A & DE 69220555 T	1-19

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

* Special categories of cited documents:

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"E"	earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search 12 May, 2009 (12.05.09)	Date of mailing of the international search report 26 May, 2009 (26.05.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	JP 1-272825 A (Kawasaki Steel Corp.), 31 October, 1989 (31.10.89), Page 3, upper right column, lines 16 to 19 (Family: none)	5-19
A	JP 2952271 B2 (Petoca, Ltd.), 20 September, 1999 (20.09.99), Claims & DE 69111335 C	1-19
A	JP 7-41372 A (Mitsubishi Chemical Corp.), 10 February, 1995 (10.02.95), Claims (Family: none)	16-19

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