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(71) Applicant: Toho Rayon Co., Ltd.
No. 3-9, Nihonbashi 3-chome
Chuo-ku Tokyo(JP)

(72) Inventor: Ogawa, Hiroyasu c/o Toho Rayon Co., Ltd.
234, Kamitokari Aza Takaishi
Nagaizumi-cho Sunto-gun Shizuoka(JP)
Inventor: Enomoto, Harumitsu c/o Toho Rayon Co., Ltd.
234, Kamitokari Aza Takaishi
Nagaizumi-cho Sunto-gun Shizuoka(JP)

(74) Representative: Hansen, Bernd, Dr.rer.nat. et al
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4 Postfach 81 04 20
D-8000 München 81(DE)

(54) High density graphite fiber and method of manufacture thereof.

(57) A graphite fiber derived from an acrylic fiber having a fiber density of not less than 1.93 g/cm^3, a strand tensile strength of not less than 350 kgf/mm^2, and a strand tensile modulus of not less than 53×10^3 kgf/mm^2, and a method for producing the grpahite fiber by carbonizing a preoxidized fiber derived from an acrylic fiber and having a fiber density of from 1.32 to 1.40 g/cm^3 to obtain a carbon fiber having a nitrogen content of not less than 1.0% by weight based on the carbon fiber weight, a fiber density of not less than 1.79 g/cm^3 and an orientation of not less than 79% at a maximum diffraction at $2\theta = 25.3\pm0.5^\circ$ in X-ray diffraction angle of the (002) plane of the graphite crystal, and graphitizing the thus-obtained carbon fiber in an inert gas at a temperature of not lower than 2,400 °C and under a tension to stretch the fiber at least 3% during the graphitization.

EP 0 374 925 A2

HIGH DENSITY GRAPHITE FIBER AND METHOD OF MANUFACTURE THEREOF

FIELD OF THE INVENTION

The present invention relates to a graphite fiber derived from polyacrylic fiber which is useful for reinforcing a composite material, particularly useful for reinforcing a composite material in the aerospace industry.

BACKGROUND OF THE INVENTION

The graphite fibers which have been used in the aerospace industry have a strand tensile modulus of 50×10^3 kgf/mm^2 at the highest and a strand tensile strength of as low as 200 kgf/mm^2. Accordingly, their use for members in the aerospace industry is limited to a very narrow range. The fibers, even when they are useful, have disadvantages in that they have to be used in a large amount or have to be used in combination with other materials, thus resulting in increased weight.

Such graphite fibers have been made according to the methods disclosed, for example, in U.S. Patent 4,321,446.

Aerospace materials which are repeatedly exposed to high temperatures and low temperatures are required to have high heat conductivity. To meet this require ment, graphite fibers need to have higher density which correlates with the heat conductivity.

Hence graphite fibers are desired to have a high density, a high strength, and a high tensile modulus. Additionally, the graphite fibers are desired to be capable of being used as pseudoisotropic composite material in use for members in the aerospace industry.

Moreover, the graphite fibers are desired to have a small filament diameter. Thus, a graphite fiber has long been desired which is composed of filaments of a small diameter, particularly not more than 7 μm in diameter, and which has a high density, a high strength and a high modulus.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a graphite fiber which is light in weight and has a high strand tensile modulus and a high strand tensile strength and further which has a high density which contributes to heat conductivity.

Another object of the present invention is to provide a graphite fiber which is suitable for producing a pseudoisotropic composite material.

According to one aspect of the present invention, there is provided graphite fiber derived from an acrylic fiber, which has a fiber density of not less than 1.93 g/cm^3, a strand tensile strength of not less than 350 kgf/mm^2, and a strand tensile modulus of not less than 53×10^3 kgf/mm^2.

According to another aspect of the present invention, there is provided a method for manufacturing a graphite fiber having a fiber density of not less than 1.93 g/cm^3, a strand tensile strength of not less than 350 kgf/mm^2, and a strand tensile modulus of not less than 53×10^3 kgf/mm^2, comprising carbonizing a preoxidized fiber derived from an acrylic fiber and having a fiber density of from 1.32 to 1.40 g/cm^3 to obtain a carbon fiber having a nitrogen content of not less than 1.0% by weight based on the carbon fiber weight, a fiber density of not less than 1.79 g/cm^3 and an orientation of not less than 79% at a maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$ in X-ray diffraction angle of the (002) plane of the graphite crystal, and graphitizing the thus-obtained carbon fiber in an inert gas at a temperature of not lower than 2,400°C and under a tension to stretch the fiber at least 3% during the graphitization.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention the fiber density, the strand tensile strength, and the tensile modulus are measured according to JIS R7601, and the diameter of filament is determined by measuring the sectional area of the filament employing scanning electromicroscopy and converting the obtained value to the true circle diameter.

According to the method of the present invention a graphite fiber having a fiber density of up to about 2.10 g/cm^3, a strand tensile strength of up to about 550 kgf/mm^2, and a strand tensile modulus of up to about 75 x 10^3 kgf/mm^2 can be obtained.

The graphite fiber of the present invention substantially consists of carbon atoms in an amount of 100% by weight. However, nitrogen atoms, oxygen atoms, and hydrogen atoms each may be present in an amount of from 0 to 0.1% by weight, and ash may be present in an amount of from 0 to 0.2% by weight based on the weight of the total weight of the grahite fiber (including such materials, when present).

The ash content is the residue of the graphite fiber after heating the graphite fiber at 650° C in the air for 300 minutes. (The heating is repeatedly conducted until the weight of the residue becomes constant.)

A fiber density of less than 1.93/cm^3 leads to decrease in the heat conductivity.

The graphite fiber of the present invention preferably is composed of a filaments of not more than 7 μm in diameter. Although the filament diameter of not more than 7 μm is desirable as mentioned above, an excessively small filament diameter (i.e., less than 0.1 μm), namely extreme fineness thereof, is undesirable because such causes a remarkable increase in fluffing of the strands in ultra-thin sheet materials. A preferred diameter is from 0.5 to 5 μm.

The number of filaments constituting a graphite fiber strand obtained according on the method of the present invention is desirably not overly large, and is preferably from 50 to 15,000 because of the required fineness of the strand. Less than 50 filaments is undesirable since it causes frequent thread breakage rendering difficult the production of thin sheet materials. The filaments constituting the strand are preferably not interlocked but are parallel with each other for producing thinner sheets. The interlocking degree of the filaments in a strand is measured by vertically hanging 300 mm long strand with a load of 0.1 g/d at the lower end thereof, perpendicularly piercing the strand with a chromium plated pin of 1 mm diameter at around the middle of the strand breadth, and measuring the distance that the pin goes down by 10 g of load for 3 minutes. The interlocking degree of the strand is represented by this distance. The interlocking degree is preferably not less than 250 mm.

The graphite fiber of the present invention can be prepared from an acrylic fiber, that is, a polyacrylonitrile fiber or a copolymer fiber composed of preferably about 90% by weight or more, and more preferably about 95% by weight or more, of acrylonitrile, and any vinyl monomers which are copolymerizable with acrylonitrile can be used as the comonomers. For instance, known comonomers can be used, including neutral monomers such as methyl acrylate, methyl methacrylate and vinyl acetate; acrylic acid, methacrylic acid, itaconic acid, maleic acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid and metal salts thereof (such as the sodium salt and potassium salt) and ammonium salts; vinylimidazole, vinylpyrimidine and derivatives thereof; and acrylamide, methacrylamide, etc. The preferred molecular weight of the polymer is about 40,000 to 200,000, more preferably about 60,000 to 150,000 calculated using Staudinger's equation.

The graphite fiber can be obtained by preoxidizing acrylic fiber, carbonizing the thus-obtained preoxidized fiber and the graphitizing the thus-obtained carbon fiber. Methods for producing carbon fiber are known, for example, in U.S. Patents 4,197,279, 4,397,831, 4,347,279, 4,474,906 and 4,522,801, and methods for producing graphite fibers are known, for example in U.S. Patent 4,321,446.

The graphite fiber of the present invention can be obtained by using a specifically selected carbon fiber and by using precisely selected conditions for obtaining the graphite fiber.

The acrylic fiber suitably comprises 50 to 15,000 filaments of a diameter of not more than 13 μm (preferably from 0.1 to 13 μm, more preferably from 0.2 to 10 μm; 0.05 to 1.5d and 0.1 to 1.0d, respectively), having a tensile strength of not less than 3 g/d (preferably of from 3 to 20 g/d, more preferably of from 5 to 15 g/d), a tensile elongation of not less than 5% (preferably from 5 to 15%, more preferably from 7 to 12%), and an orientation degree of not less than 88% (preferably of from 88 to 95%, more preferably of from 90 to 95%) measured at the diffraction angle range of $2\theta = 17.3 \pm 0.30^\circ$ where the maximum diffraction intensity is exhibited in X-ray diffraction. Such an acrylic fiber, can be obtained referring to U.S. Patent Application Serial No. 845,167 (corresponding to DE-A1 36 10 517) The acrylic fiber is preoxidized by heating in air at a temperature below the heat decomposition temperature of the fiber (usually at from 200 to 350° C) under a tension preferably of from 70 to 200 mg/d (more preferably of from 100 to 150 mg/d) for preferably from 5 to 120 minutes (more preferably of from 10 to 60 minutes) to give a fiber density of from 1.32 to 1.40 g/cm^3 (preferably from 1.32 to 1.37 g/cm^3). Subsequently, the thus obtained preoxidized fiber is carbonized in an inert atmosphere (nitrogen, argon or helium) at a temperature preferably of from 1,100 to 1,430° C (more preferably of from 1,200 to 1,400° C) for preferably from 0.5 to

10 minutes (more preferably from 1 to 5 minutes) under a tension to stretch the fiber (in an extent preferably of from 5 to 20%, more preferably from 8 to 12%) so as to result in a nitrogen content of at least 1.0% (preferably of from 1.0 to 8%, more preferably of from 3 to 5%) by weight in the fiber, an orientation of not less than 79% (preferably of from 79 to 84%, more preferably of from 80 to 84%) measured at a maximum diffraction intensity at $2\theta = 25.3 \pm 0.5^\circ$ (X-ray diffraction angle of the (002) plane of graphite crystal), and a fiber density of at least 1.79 g/cm^3 (preferably from 1.79 to 1.85 g/cm^3, more preferably from 1.81 to 1.85 g/cm^3).

Thereafter the thus obtained carbon fiber is stretched at least 3% (preferably from 5 to 15%, more preferably 5 to 10%) during graphitizing in an inert gas atmosphere (argon, helium or nitrogen, preferably argon or helium) at a temperature of 2,400 °C or higher (preferably of from 2,400 to 3,300 °C, more preferably of from 2,600 to 3,300 °C) to produce a graphite fiber. The time period for heating (graphitizing) is usually from about 0.1 to 10 minutes. The graphitization is conducted until the density of the fiber becomes at least 1.93 g/cm^3. The thus obtained graphite fiber has an orientation degree (measured as above at $2\theta = 25.3 \pm 0.5^\circ$), preferably of from 85 to 98%, more preferably from 90 to 98%.

Among the above manufacturing conditions, the fiber density of the preoxidized fiber, the nitrogen content, the orientation degree, the density of the carbon fiber, the graphitization temperature of 2,400 °C or higher and the elongation ratio must be met to provide the intended graphite.

By employing the graphite fiber of the present invention in combination with a known resin, unidirectional composite materials, textile composite materials, and pseudoisotropic composite materials by multidirectional lamination can be prepared.

The composite materials reinforced by the graphite fiber of the present invention will enable a weight reduction and thus a speed increase of flying objects, satellites, and space stations etc., in the aerospace field, and similar results with respect to rotating bodies, travelling bodies, etc., in other technical fields.

Examples are shown below together with comparative examples. Unless otherwise mentioned, "%" and "parts" are based on weight in the examples.

EXAMPLE 1

Various graphite fibers were prepared from an acrylic fiber (filament: 0.5 denier, number of filaments: 6000, tensile strength: 6.8 g/d, tensile elongation: 11%, orientation degree: 90.5% at a diffraction angle of the diffraction peak at $2\theta = 17.3 \pm 0.3^\circ$ in X ray diffraction) composed of 98% of acrylonitrile, 1.5% of methyl acrylate (the molecular weight of the acrylonitrile copolymer was 75,000), and 0.5% of itaconic acid, under the conditions shown in Table 1 regarding the preoxidation treatment (in air, 250 °C, tension: 150 mg/d), the carbonization (in nitrogen gas, 3 minutes), and the graphitization (in argon, 3 minutes).

A prepreg containing fiber in an amount of 150 g/m^2 with a resin content of 37% (based on the weight of the prepreg) was prepared from the thus obtained graphite fiber and a resin component constituted of 50 parts of an epoxy resin: Epikote 828 (made by Yuka Shell Epoxy K.K., bisphenol A diglycidyl ether having an epoxy equivalent of from 184 to 194), 50 parts of Epikote 1002 (made by Yuka Shell Epoxy K.K., bisphenol A diglycidyl ether having an epoxy equivalent of from 600 to 700) and 3 parts of dicyandiamide, by arranging the graphite fiber unidirectionally.

The prepreg was laminated and compression molded at 130 °C for 2 hours under a pressure of 7 kgf/cm^2 to produce a composite material in the form of a plate.

The tensile characteristics and heat conductivity of the plate were measured. Table 2 shows the results. Table 2 shows that the composite materials produced employing the graphite fiber of the present invention have high strength, high modulus and excellent heat conductivity.

TABLE 1

	Sample No.					
	1*	2*	3**	4**	5**	6**
Preoxidation Time (min.)	48	48	48	55	42	35
Preoxidized Fiber Density	1.32	1.32	1.32	1.35	(1.31)	1.30
Carbonization Conditions						
Temperature (°C)	1380	1380	1380	1380	1380	1450
Elongation (%)	8	8	1	8	8	8
Properties of Carbon Fiber						
Orientation (%)	82	82	(78)	81	80	80
Nitrogen Content (%)	3.5	3.5	3.5	3.5	3.5	(0.8)
Density (g/cm³)	1.83	1.83	1.80	(1.78)	1.84	1.82
Graphitization Conditions						
Temperature (°C)	2880	2880	2880	2880	2880	2880
Elongation (%)	7	3	7	6	7	7
Properties of Graphite Fiber						
Tensile Strength(kgf/mm²)	380	355	(300)	383	(283)	(305)
Tensile Modulus (x10³ kgf/mm²)	58.5	53.0	57.3	56.8	56.9	57.7
Fiber Density (g/cm³)	1.96	1.96	1.96	(1.90)	1.96	1.96
Fiber diameter (um)	4.6	4.7	4.8	4.5	5.3	4.5
Orientation (%)	93	92	89	91	90	90
Notes:						

* : Invention

**: Comparative

1) Filament denier of the acrylic fiber used for preparation of Sample 5 was 0.65

2) Values in the parenthesis in Tables 1 and 2 are outside the present invention.

TABLE 2

(Properties of Composite (ASTM D-3039)				
Sample No.	Tensile Strength (kgf/mm^2)	Tensile Modulus (x10^3 kgf/mm^2)	Heat Conductivity* (W/m° K)	Evaluation (Comparison with Sample 1)
1 (Invention)	217	34.0	64	-
2 (Invention)	201	31.0	64	Tensile strength and tensile modulus being slightly low.
3 (Comparative)	165	33.5	64	Tensile strength being low.
4 (Comparative)	210	33.2	60	Heat conductivity being low.
5 (Comparative)	120	33.4	64	Tensile strength and being low.
6 (Comparative)	143	33.6	64	Tensile strength being low.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A graphite fiber derived from an acrylic fiber having a fiber density of not less than 1.93 g/cm^3, a strand tensile strength of not less than 350 kgf/mm^2, and a strand tensile modulus of not less than 53×10^3 kgf mm^2

2. The graphite fiber as in Claim 1, wherein the graphite fiber has a filament diameter of not more than 7 μm.

3. The graphite fiber as in claim 1, wherein said fiber density is from 1.93 to 2.10 g/cm^3.

4. the graphite fiber as in claim 1, wherein asid strand tensile strength is from 350 to 550 kgf/mm^2.

5. The graphite fiber as in claim 1, wherein said strand tensile modulus is from 53 x 10^3 to 75 x 10^3 kgf mm^2.

6. The graphite fiber as in claim 1, wherein the filament diameter is from 0.1 to 7 μm.

7. The graphite fiber as in claim 1, wherein the graphite fiber consists of 99.5 to 100% by weight of carbon atoms, less than 0.1% by weight of each of, nitrogen atoms, oxygen atoms, and hydrogen atoms, and less than 0.2% by weight of ash.

8. The graphite fiber as in claim 1, wherein the graphite fiber has an orientation of from 85 to 98% at a maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$, X-ray diffraction angle, of (002) plane of the graphite crystal.

9. The graphite fiber as in claim 1, wherein the density is from 1.93 to 2.10 g/cm^3, the strand tensile strength is from 350 to 550 kgf/mm^2, the strand tensile modulus is from 53 x 10^3 to 75 x 10^3 kgf/mm^2, the graphite fiber consists of from 99.5 to 100% by weight of carbon atoms, less than 0.1% by weight of each of nitrogen atoms, oxygen atoms, and hydrogen atoms, and less than 0.2% by weight of ash, and the graphite fiber has an orientation of from 85 to 98% at a maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$, X-ray diffraction angle, of (002) plane of the graphite crystal.

10. A method for manufacturing a graphite fiber having a fiber density of not less than 1.93 g/cm^3, a strand tensile strength of not less than 350 kgf/mm^2, and a strand tensile modulus of not less than 53×10^3 kgf/mm^2, comprising carbonizing a preoxidized fiber derived from an acrylic fiber and having a fiber density of from 1.32 to 1.40 g/cm^3 to obtain a carbon fiber having a nitrogen content of not less than 1.0% by weight based on the carbon fiber weight, a fiber density of not less than 1.79 g/cm^3 and an orientation of not less than 79% at a maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$ in X-ray diffraction angle of the (002) plane of the graphite crystal, and graphitizing the thus-obtained carbon fiber in an inert gas at a temperature of not lower than 2,400°C and under a tension to stretch the fiber at least 3% during the graphitization.

11. The method for manufacturing a graphite fiber as in claim 10, wherein the carbon fiber is stretched by 3% to 15% during the graphitization.

12. The method for manufacturing a graphite fiber as in claim 10, wherein the nitrogen content of the carbon fiber is from 0.5 to 8% by weight.

13. The method for manufacturing a graphite fibers as in claim 10, wherein the carbon fiber has an orientation of from 79 to 84% at the maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$, X-ray diffraction angle, of (002) plane of the graphite crystal.

14. The method for manufacturing a graphite fiber as in claim 10, wherein the fiber density of the carbon fiber is from 1.79 to 1.85 g/cm^3.

15. The method for manufacturing a graphite fiber as in claim 10, wherein the carbon fiber comprises a strand consisting of from 50 to 15,000 filaments.

16. The method for manufacturing a graphite fiber as in claim 10, wherein the acrylic fiber is a polyacrylonitrile fiber or a copolymer fiber composed of not less than 90% by weight of acrylonitrile.

17. The method for manufacturing a graphite fiber as in claim 10, wherein the acrylic fiber has a filament diameter of from 0.1 to 13 μm.

18. The method for manufacturing a graphite fiber as in claim 10, wherein the carbon fiber is derived from a aryclic fiber having a tensile strength of not less than 3 g/d, an tensile elongation of not less than 5%, and an orientation degree of not less than 88% measured at the X-ray diffraction angle of $2\theta = 17.3 \pm 0.3^\circ$.

19. The method for manufacturing a graphite fiber as in claim 10, wherein the graphitizing temperature is from 2,400 to 3,300°C.

20. The method for manufacturing a graphite fiber as in claim 18, wherein the carbon fiber is obtained by preoxidizing said acrylic fiber in air at a temperature of from 200 to 350 ° C under a tension of from 70 to 200 mg/d until the fiber density reaches 1.33 to 1.40 g/cm^3, and then the thus obtained preoxidized fiber is carbonized in an inert atmosphere at a temperatue of from 1,100 to 1,430 ° C while under a stretching condition so as to result in the orientation degree of from 79% to 84% at the maximum diffraction at $2\theta = 25.3 \pm 0.5^\circ$, X-ray diffraction angle, of (002) plane of the graphite crystal, until fiber density becomes least 1.79 to 1.85 g/cm^3 and the nitrogen content of from 1.0 to 8% by weight.

21. The method for manufacturing a graphite fiber as in claim 20, wherein carbonizing is conducted under a stretching condition to stretch the fiber in an extent of from 5 to 20%.