



(11)

EP 4 682 300 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
21.01.2026 Bulletin 2026/04

(51) International Patent Classification (IPC):
D02G 3/36 ^(2006.01) **D01F 9/12** ^(2006.01)
D02G 3/16 ^(2006.01)

(21) Application number: **24770892.8**

(52) Cooperative Patent Classification (CPC):
D01F 9/12; D02G 3/16; D02G 3/36

(22) Date of filing: **12.03.2024**

(86) International application number:
PCT/JP2024/009603

(87) International publication number:
WO 2024/190787 (19.09.2024 Gazette 2024/38)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

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(30) Priority: **16.03.2023 JP 2023042047**

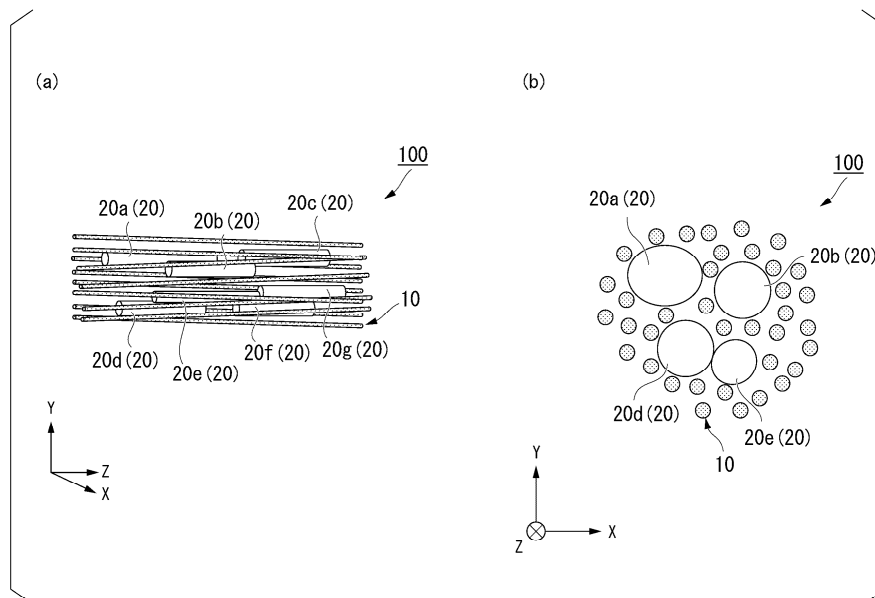
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(54) **CONTINUOUS CONJUGATE FIBERS, AND PRODUCTION DEVICE AND PRODUCTION METHOD FOR CONTINUOUS CONJUGATE FIBERS**

(57) A conjugate material includes: a plurality of fibrous materials; and a plurality of carbon nanotube fibers

which consists of carbon nanotubes and arranged to surround the plurality of fibrous materials.

FIG. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a continuous conjugate fiber, a continuous conjugate fiber production device, and a continuous conjugate fiber production method.

[0002] Priority is claimed on Japanese Patent Application No. 2023-042047, filed March 16, 2023, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] Carbon fibers are used in a variety of applications because they are lightweight, have a high specific strength, and have excellent mechanical properties. For example, carbon fiber reinforced plastic (CFRP) which consists of carbon fiber and matrix resin is used in aerospace applications, sports and leisure applications such as automobiles, wind power generators, fishing rods, golf shafts, and tennis rackets, and electronic device applications such as housings of notebook computers, tablets, and smartphones. In recent years, the amount of CFRP used for various applications has become enormous.

[0004] As a method of producing CFRP, there is known a method in which carbon fiber bundles are cut, the carbon fiber bundles are impregnated with resin, and then the resin-impregnated carbon fiber bundles are formed into a sheet (for example, Patent Document 1). The resin-impregnated carbon fiber bundles are also called prepregs.

[0005] While carbon fiber is used in a wide range of applications as described above, disposal of fiber wastes generated during the process of cutting prepreg and unnecessary prepreg or carbon fiber becomes an issue. Carbon fiber is typically buried because the carbon fiber is non-combustible and non-rotting. As described above, it is expected that aircraft, automobiles, wind turbines, and other machines manufactured using large amounts of CFRP will reach the end of their lifespan over time. Therefore, it is expected that a large amount of waste of CFRP used in these machines will be generated in the future. As described above, since these materials are not only non-combustible and non-rotting, but also have a large volume, burying all these materials would be considered a large environmental burden when disposing of such waste. For this reason, there is a demand for reusing CFRP, and various methods for reusing CFRP are being considered. However, an effective approach for reusing CFRP has not yet been found.

[0006] In recent years, there has been a demand to avoid waste of prepreps and carbon fibers as much as possible in order to prevent underground pollution caused by landfill disposal. For example, as means for recovering carbon fibers from CFRP, there is known a method in which CFRP is controlled at a predetermined temperature in an atmosphere of a predetermined oxy-

gen concentration to pyrolyze plastic and recover carbon fibers (for example, Patent Document 2).

[0007] In addition, there is known a method of recovering recycled carbon fiber (rCF) that exhibits good physical properties from CFRP. In the automobile industry, the Automobile Recycling Law has been established, and it is necessary to recycle parts and materials from discarded automobiles. In Japan, there are carbon fiber manufacturers and automobile companies with the world's top market share, and the demand for reuse of CFRP is particularly high.

Citation List

15 Patent Documents

[0008]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2010-163536

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. H6-99160

SUMMARY OF INVENTION

Technical Problem

[0009] In order to effectively prevent underground contamination, etc., it is necessary to reuse the prepreg and carbon fiber scraps recovered by the above methods in some form. The recovered carbon fiber and prepreg scraps are also called recycled carbon fibers. Regarding the carbon fibers recovered by the method described in Patent Document 2, they are often too long and entangled in a fibrous form or too short. Accordingly, although it is possible to recover them as carbon fibers, it is considered that they are less likely to be reused. For this reason, it has been proposed to crush the recovered carbon fibers and mix them into rubber or thermoplastic resins to improve their abrasion resistance, or to mix them into cement, mortar, concrete, etc. to improve their mechanical properties (Patent Document 2).

[0010] Thus, even if the carbon fibers contained in the CFRP of Patent Document 1 are recovered by the process of Patent Document 2, the recovered carbon fibers are either too long and entangled or too short. Therefore, the recovered carbon fiber is not reused as carbon fiber, but as an additive to add specific functions. As a result, it was not possible to use the excellent specific strength exhibited by the fibrous form of recycled carbon fiber, and in order to obtain new carbon fiber, it was necessary to produce carbon fiber again in zero base. Additionally, in other fields such as aramid fibers, recycled fibrous materials have generally not been used in a state in which the fibrous form is maintained.

[0011] The present invention has been made in view of the above-described circumstances and an object thereof is to provide a continuous conjugate fiber capable of

using a fibrous material in a fibrous form, a continuous conjugate fiber production device, and a continuous conjugate fiber production method.

Solution to Problem

[0012]

(1) A continuous conjugate fiber according to an aspect of the present invention includes: a plurality of fibrous materials; and a plurality of carbon nanotube fibers which are arranged to surround the plurality of fibrous materials.

(2) In the continuous conjugate fiber of (1), a tensile strength of a single fibrous material may be lower than a tensile strength of a single carbon nanotube fiber constituting the plurality of carbon nanotube fibers.

(3) In the continuous conjugate fiber of (1) or (2), the fibrous material may comprise carbon fiber.

(4) In the continuous conjugate fiber of (1) to (3), each of the plurality of carbon nanotube fibers may comprise a plurality of carbon nanotubes, and the plurality of carbon nanotubes may be bonded to each other by van der Waals forces.

(5) In the continuous conjugate fiber of (1) to (4), the fibrous material may have a diameter of 5 μm or more and 50 μm or less, and the carbon nanotube fiber may have a diameter of 4 nm or more and 50 nm or less.

(6) In the continuous conjugate fiber of (1) to (5), the plurality of carbon nanotube fibers may constitute twisted yarns.

(7) A continuous conjugate fiber production device according to an aspect of the present invention includes: an adding unit which adds a plurality of fibrous materials to a plurality of carbon nanotube fibers; and a forming unit which bundles the plurality of carbon nanotube fibers having the plurality of fibrous materials added thereto to form a fibrous continuous conjugate fiber.

(8) The production device of (7) may further include: a twisting unit which twists the continuous conjugate fibers.

(9) A continuous conjugate fiber production method according to an aspect of the present invention includes: an adding step of adding a plurality of fibrous materials to a plurality of carbon nanotube fibers; and a forming step of bundling the plurality of carbon nanotube fibers having the plurality of fibrous materials added thereto to form a fibrous continuous conjugate fiber.

(10) In the continuous conjugate fiber production method of (9), in the adding step, the plurality of carbon nanotube fibers may be a unidirectionally oriented film.

(11) In the continuous conjugate fiber production method of (9) or (10), a strength of a single fibrous

material may be lower than a strength of a single carbon nanotube fiber constituting the plurality of carbon nanotube fibers.

(12) In the continuous conjugate fiber production method of (9) to (11), the fibrous material may comprise carbon fiber.

(13) In the continuous conjugate fiber production method of (9) to (12), in the adding step, an airflow may be generated in a closed space, and the plurality of fibrous materials may be added to the plurality of carbon nanotube fibers by the airflow.

(14) In the continuous conjugate fiber production method of (9) to (13), in the adding step, the plurality of carbon nanotube fibers may be arranged two-dimensionally, and the plurality of fibrous materials may be placed on the plurality of carbon nanotube fibers arranged two-dimensionally.

(15) In the continuous conjugate fiber production method of (9) to (14), in the adding step, a plurality of guide members arranged with gaps therebetween along a longitudinal direction of the plurality of carbon nanotube fibers may be arranged above the plurality of carbon nanotube fibers arranged two-dimensionally, and the plurality of fibrous materials may be placed on the plurality of carbon nanotube fibers through the gaps between the plurality of guide members.

(16) In the continuous conjugate fiber production method of (9) to (15), in the adding step, a dispersion liquid in which the plurality of fibrous materials are dispersed may be prepared, and the plurality of carbon nanotube fibers may be immersed in the dispersion liquid to add the plurality of fibrous materials to the plurality of carbon nanotube fibers.

(17) The continuous conjugate fiber production method of (9) to (16) may further include: a twisting step of twisting the continuous conjugate fibers after the forming step. Advantageous Effects of Invention

[0013] According to the present invention, it is possible to provide a continuous conjugate fiber capable of using a fibrous material in a fibrous form, a continuous conjugate fiber production device, and a continuous conjugate fiber production method.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

[FIG. 1] A diagram showing a continuous conjugate fiber according to an embodiment of the present invention, where FIG. 1(a) is a perspective view schematically showing an example of a configuration of a continuous conjugate fiber according to an embodiment of the present invention and FIG. 1(b) is a cross-sectional view schematically showing an example of a configuration of a continuous conjugate fiber according to an embodiment of the present

invention.

[FIG. 2] A perspective view schematically showing a configuration of a modified example of the continuous conjugate fiber of FIG. 1.

[FIG. 3] A perspective view schematically showing a configuration of another modified example of the continuous conjugate fiber of FIG. 1.

[FIG. 4] A flowchart of a continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 5] A flowchart of a continuous conjugate fiber production method according to a modified example of FIG. 4.

[FIG. 6] A perspective view showing an example of a configuration of a device used in an adding step of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 7] A schematic view illustrating an example of a method of producing a unidirectionally oriented film.

[FIG. 8] A conceptual diagram illustrating the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 9] A diagram illustrating a modified example of FIG. 8 of the adding step of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 10] A diagram illustrating a modified example of FIG. 8 of the adding step of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 11] A conceptual diagram illustrating a modified example of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 12] A conceptual diagram illustrating a modified example of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 13] A conceptual diagram illustrating a modified example of the continuous conjugate fiber production method according to an embodiment of the present invention.

[FIG. 14] FIG. 14 is an SEM image of a continuous conjugate fiber of Example 1.

[FIG. 15] FIG. 15 is An SEM image of a continuous conjugate fiber of Example 2.

[FIG. 16] FIG. 16 is An SEM image of a fibrous material of Comparative Example 1.

[FIG. 17] An SEM image of the continuous conjugate fiber of Example 1 different from that of FIG. 14.

[FIG. 18] A graph showing the strength of the continuous conjugate fiber of Example 1.

[FIG. 19] A graph showing the strength of the continuous conjugate fiber of Example 2.

[FIG. 20] A graph showing the strength of a recycled carbon fiber of Comparative Example 1.

[FIG. 21] An SEM image of a continuous conjugate

fiber of Example 4.

[FIG. 22] A graph showing the strength of a continuous conjugate fiber of Example 3.

[FIG. 23] A graph showing the strength of the continuous conjugate fiber of Example 4.

[FIG. 24] An SEM image of a continuous conjugate fiber of Example 5.

[FIG. 25] A graph showing the strength of the continuous conjugate fiber of Example 5.

[FIG. 26] An SEM image of a continuous conjugate fiber of Example 6.

[FIG. 27] A graph showing the strength of the continuous conjugate fiber of Example 6.

[FIG. 28] A diagram showing a correlation between diameter and strength of the continuous conjugate fiber of Example 6.

DESCRIPTION OF EMBODIMENTS

[0015] Hereinafter, an example of an embodiment of the present invention will be described in detail with reference to the drawings. Furthermore, in the drawings used in the following description, characteristic parts of the present invention may be enlarged for the sake of convenience in order to make the characteristics of the present invention easier to understand. Therefore, the dimensional ratios of each component may differ from the actual ones.

[Continuous conjugate fiber]

[0016] FIG. 1 is a diagram showing a continuous conjugate fiber according to an embodiment of the present invention, FIG. 1(a) is a perspective view showing an example of a configuration of the continuous conjugate fiber according to an embodiment of the present invention, and FIG. 1(b) is a cross-sectional view showing an example of a configuration of the continuous conjugate fiber according to an embodiment of the present invention. FIG. 1(a) is a partially enlarged view of the continuous conjugate fiber. A continuous conjugate fiber 100 shown in FIGS. 1(a) and 1(b) includes a plurality of fibrous materials 20 and a plurality of carbon nanotube fibers 10 arranged to surround the plurality of fibrous materials 20. The continuous conjugate fiber 100 preferably includes the plurality of carbon nanotube fibers 10 and the plurality of fibrous materials 20. For example, the plurality of fibrous materials 20 are oriented in substantially the same direction. For example, as shown FIG. 1(a), the fibrous material 20 is provided along the longitudinal direction of the carbon nanotube fiber 10. In the continuous conjugate fiber 100, the plurality of fibrous materials 20 are preferably not exposed to the outside. In the continuous conjugate fiber 100, the plurality of carbon nanotube fibers 10 are arranged to surround fibrous materials 20a, 20b, 20c, 20d, 20e, 20f, and 20g.

[0017] For example, as shown in FIG. 1(b), the outer periphery of the fibrous material 20 is surrounded by the

plurality of carbon nanotube fibers 10. The carbon nanotube fiber 10 may be inclined relative to each fibrous material 20. The plurality of fibrous materials 20 may be in direct contact with each other or may be indirectly in contact with each other via the carbon nanotube fibers 10 or the like.

[0018] In the continuous conjugate fiber 100, the fibrous materials 20d, 20e, 20f, and 20g are arranged such that their ends in the longitudinal direction are offset. Each of the fibrous materials 20d, 20e, 20f, and 20g is arranged such that, for example, the ends in the longitudinal direction are shifted and are in contact with other fibrous materials in the radial direction. Specifically, the fibrous material 20d is in contact with the fibrous material 20e, and the fibrous material 20e is in contact with the fibrous material 20f and the fibrous material 20g. When the fibrous materials 20 are in contact with each other, for example, they are attracted to each other by van der Waals forces, and are bonded by van der Waals forces. When van der Waals bonding is used, no adhesives are required or used. The fibrous material 20 is preferably disposed in close proximity to other fibrous materials even if the fibrous material is not in contact with other fibrous materials. That is, it is preferable that the distance between the ends of the fibrous materials 20 that are spaced apart and that are closest to each other in the longitudinal direction is small.

[0019] Each carbon nanotube fiber 10 is mainly composed of carbon atoms. For example, the carbon nanotube fibers 10 of this embodiment comprises a plurality of carbon nanotubes, each of which consists of a unit fiber formed by carbon atoms bonded in a lattice pattern, and which are bonded to each other by intermolecular forces called van der Waals forces. The carbon nanotube fibers 10 have a higher strength per unit area than carbon fibers such as recycled carbon fibers, are composed of carbon atoms and bonded by van der Waals forces like carbon fibers such as recycled carbon fibers, which are an example of a material that can be used as the fibrous material 20, and have no adhesive layer or surface covering layer. Therefore, the carbon nanotube fibers 10, which are composed of carbon atoms, have a high degree of adhesion to the recycled carbon fibers, and are less likely to peel off than fibers made of other materials. Further, it is possible to produce the continuous conjugate fibers 100 that are as strong as or stronger than the original carbon fibers by surrounding recycled carbon fibers, which are often short and irregular in length, as the fibrous material 20 with carbon nanotube fibers 10, which are thinner and have a higher specific strength. Further, the continuous conjugate fiber 100 can be produced more cheaply, and the cost of the continuous conjugate fiber 100 can be decreased by replacing a part of the expensive carbon nanotube fibers 10 with recycled carbon fibers. Furthermore, even if recycled carbon fibers are not used as the fibrous materials 20, it is possible to produce the continuous conjugate fiber 100 which is as strong as or stronger than the original fibrous material by

surrounding the recycled carbon fibers with the carbon nanotube fibers 10 which are thinner and have a higher specific strength.

[0020] The diameter of the carbon nanotube fiber is, for example, 5 nm or more and 50 nm or less, and may be 4 nm or more and 50 nm or less.

[0021] The fibrous material 20 is preferably comprises carbon fibers. As specific examples, the fibrous material 20 consists of carbon fibers such as PAN-based carbon fibers and pitch-based carbon fibers, glass fibers, and the like and preferably consists of carbon fibers. From the viewpoint of suppressing underground contamination, it is preferable that the carbon fiber is a carbon fiber recovered from fiber waste of CFRP, prepreg, or carbon fiber. The carbon fibers described above are called recycled carbon fibers. The recycled carbon fibers used as the fibrous material 20 are preferably ones from which resin has been removed by heat treatment or chemical treatment as disclosed in Patent Document 2. Other fibrous materials such as glass fiber other than carbon fiber may also be used. As with carbon fiber, extremely short fibrous materials other than carbon fiber are produced during the production process and are discarded rather than reused, so there was a need for ways to use them.

[0022] The tensile strength of the single fibrous material 20 is, for example, lower than the tensile strength of the single carbon nanotube fiber 10 constituting the plurality of carbon nanotube fibers. The tensile strength of the single carbon nanotube fiber 10 is higher than the tensile strength of the single fibrous material 20, which has the effect of improving the strength of the continuous conjugate fiber 100. Most of the recycled carbon fibers on the market are short in length, but it is believed that the above effect can be obtained even when short recycled carbon fibers are used. The length of the recycled carbon fibers used is preferably 2 μm or more, and more preferably 3 μm or more. The difference between the minimum and maximum lengths of the recycled carbon fibers used may be 10 μm or less, or may be 5 μm or less.

[0023] The tensile strength of the single fibrous material 20 and the tensile strength of the single carbon nanotube fiber 10 are measured by a method conforming to JIS R 7606:2000 (MOD). The single fibrous material 20 means one strand of the fibrous materials 20, and tensile strength measurements are made on one strand of the fibrous materials. Similarly, the single carbon nanotube fiber 10 means one carbon nanotube fiber 10, and the tensile strength is measured for one carbon nanotube fiber.

[0024] The diameter of the fibrous material 20 may be, for example, 3 μm or more and 100 μm or less, and may be 5 μm or more and 50 μm or less. A large diameter of the fibrous material 20 increases the strength of the continuous conjugate fiber 100. On the other hand, since the diameter of the fibrous material 20 is small, the fibrous material 20 is less likely to protrude outward from the carbon nanotube fibers 10. Therefore, since the diameter

of the fibrous material 20 is small, the durability of the structure in which the plurality of fibrous materials 20 are arranged to be surrounded by the plurality of carbon nanotube fibers 10 is improved, and the tensile strength of the continuous conjugate fiber is likely to be maintained.

[0025] The diameter of the continuous conjugate fiber 100 is, for example, 5 μm or more and 150 μm or less, and may be 15 μm or more and 100 μm or less, 15 μm or more and 50 μm or less, or 15 μm or more and 25 μm or less. Further, the diameter of the continuous conjugate fiber 100 may be 5 μm or more and 20 μm or less, or 5 μm or more and 10 μm or less. Here, the diameter of the continuous conjugate fiber 100 is larger than the diameter of the fibrous material. The diameter of the continuous conjugate fiber 100 has a high degree of freedom, and the strength becomes higher as the diameter of the fiber that can bear the same load becomes smaller. Further, when the volume of continuous conjugate fibers is small, the volume fraction of fibrous material relative to the volume is improved. Therefore, for example, when recycled carbon fiber is used as the fibrous material 20, the volume ratio of recycled carbon fiber in the continuous conjugate fiber can be increased, thereby obtaining the advantage of increasing the ratio of recycled carbon fiber that is reused in application.

[0026] The specific gravity, represented by the ratio of the mass M_f of the fibrous material 20 to the mass M_{CNT} of the carbon nanotube fiber 10 (M_f/M_{CNT}), is, for example, 0.004 or more and 100 or less, preferably 0.71 or more and 40 or less, and may be 0.71 or more and 20 or less.

[0027] The continuous conjugate fiber of the present invention is not limited to the continuous conjugate fiber according to the above-described embodiment, and may have other configurations. For example, the configuration shown in FIG. 2 may be used. FIG. 2 is a perspective view schematically showing a configuration of a modified example of the continuous conjugate fiber of FIG. 1. FIG. 2 is a partially enlarged view of the continuous conjugate fiber. The continuous conjugate fiber 101 shown in FIG. 2 includes the plurality of fibrous materials 20 and the plurality of carbon nanotube fibers 10 formed in a spiral shape surrounding the plurality of fibrous materials 20. In FIG. 2, for convenience of description, there are gaps between the adjacent carbon nanotube fibers 10, and a part of the fibrous material 20 surrounded by the plurality of carbon nanotube fibers 10 is visible, but it is preferable that the adjacent carbon nanotube fibers 10 are in contact with each other. In the continuous conjugate fiber 101, the plurality of carbon nanotube fibers 10 are, for example, twisted yarns. Further, the continuous conjugate fiber 101 is also a twisted yarn in which the plurality of carbon nanotube fibers 10 and the plurality of fibrous materials 20 are twisted together.

[0028] The orientation direction of the plurality of fibrous materials 20 is, for example, a direction along the axial direction of the plurality of carbon nanotube fibers 10 formed in a spiral shape. The plurality of carbon nanotube

fibers 10 are formed, for example, in a single layer around the outer periphery of the plurality of fibrous materials 20, or may be formed in multiple layers. Further, the plurality of carbon nanotube fibers 10 are preferably formed so that the plurality of fibrous materials 20 are not exposed to the outside.

[0029] The angle of the carbon nanotube fiber 10 relative to the longitudinal direction of the continuous conjugate fiber 101 is, for example, 0° or more and 90° or less, and preferably 0° or more and 45° or less. The angle may be 10° or more and 30° or less. The angle of the carbon nanotube fiber 10 formed relative to the longitudinal direction of the continuous conjugate fiber 101 is determined by measuring the angle between the side wall of the continuous conjugate fiber and the carbon nanotube fiber 10 at 10 points in a scanning electron microscope image of the continuous conjugate fiber when a part of the carbon nanotube fiber 10 is exposed or can be confirmed by a scanning electron microscope, and taking the average of the angles.

[0030] In the cross section of the continuous conjugate fiber 101, the carbon nanotube fibers 10 are, for example, located radially outward from the fibrous material 20 located near the axial center, and are formed in at least one layer, and may also be formed in multiple layers.

[0031] When the plurality of carbon nanotube fibers 10 are formed in a spiral shape around the outer periphery of the plurality of fibrous materials 20, the longitudinal direction of the fibrous material 20 is oriented along the axial direction of the plurality of carbon nanotube fibers 10 surrounding the fibrous material 20. From the viewpoint of increasing strength, it is also preferable that the continuous conjugate fiber has a structure in which a plurality of carbon nanotubes are formed in a spiral shape around the outer periphery of the plurality of fibrous materials.

[0032] FIG. 3 is a perspective view schematically showing a configuration of another modified example of the continuous conjugate fiber of FIG. 1. FIG. 3 is a partially enlarged view of the continuous conjugate fiber. A continuous conjugate fiber 102 shown in FIG. 3 includes a plurality of fibrous materials 20a, 20b, and 20c and the plurality of carbon nanotube fibers 10 arranged to surround the plurality of fibrous materials 20a to 20c. In the continuous conjugate fiber 102, the plurality of fibrous materials 20a, 20b, and 20c are arranged in a row along the axial direction of the plurality of carbon nanotube fibers 10 that are formed in a spiral shape.

[0033] When the plurality of fibrous materials 20a, 20b, and 20c are arranged in a row as in the continuous conjugate fiber 102, the density of the fibrous materials 20 in the continuous conjugate fiber 102 is increased. In the continuous conjugate fiber 102, the average number of fibrous materials 20 in a cross section intersecting the axial direction of the spiral carbon nanotube fiber 10 does not necessarily have to be one or less. In the continuous conjugate fiber 102, the average number of fibrous materials 20 in a cross section intersecting the axial direction of the spiral carbon nanotube fiber 10 is preferably 5 or

less. The intersecting cross section is preferably a cross section perpendicular to the axial direction of the spiral carbon nanotube fiber 10. The average number is calculated by observing five cross sections of the same continuous conjugate fiber that intersect with the axial direction of the spiral carbon nanotube fibers 10 using an electron microscope, and taking the average number of fibrous materials 20 in each cross section.

[Continuous conjugate fiber production method]

[0034] Next, an example of a continuous conjugate fiber production method will be described. FIG. 4 is a flowchart of the continuous conjugate fiber production method according to an embodiment of the present invention. The continuous conjugate fiber production method according to this embodiment includes an adding step of adding a plurality of fibrous materials to a plurality of carbon nanotube fibers and a forming step of bundling a plurality of carbon nanotube fibers having the plurality of fibrous materials added thereto to form a fibrous continuous conjugate fiber.

[0035] FIG. 5 is a flowchart of a continuous conjugate fiber production method according to a modified example of FIG. 4. The continuous conjugate fiber production method may further include a twisting step of twisting the continuous conjugate fiber after the forming step. FIG. 6 is a conceptual diagram illustrating the continuous conjugate fiber production method according to an embodiment of the present invention.

[0036] In the continuous conjugate fiber production method according to this embodiment, the plurality of fibrous materials 20 are added to the plurality of carbon nanotube fibers 10 (FIG. 6, adding step). For example, it is preferable to use a unidirectionally oriented film 10W as the two-dimensionally arranged carbon nanotube fibers 10 in which the plurality of carbon nanotube fibers 10 are arranged two-dimensionally and the plurality of fibrous materials 20 are placed on the two-dimensionally arranged carbon nanotube fibers 10 from the viewpoint of easily adding the fibrous materials 20.

[0037] The unidirectionally oriented film 10W is formed, for example, by the following procedure. FIG. 7 is a schematic view illustrating an example of a method of producing the unidirectionally oriented film. A film in which carbon nanotubes are oriented in one direction is also called a web (CNT web).

[0038] First, the plurality of carbon nanotubes 15 oriented perpendicularly to the substrate S are grown by chemical vapor deposition. The formation of the plurality of carbon nanotubes 15 oriented perpendicularly to the substrate S may be performed, for example, after forming a metal catalyst on the substrate S in advance by sputtering or the like. The plurality of carbon nanotubes 15 oriented perpendicularly to the substrate are densely formed on the substrate S. Such a plurality of carbon nanotubes 15 oriented perpendicularly to the substrate is called a CNT forest, and is indicated by the symbol f in

FIG. 7.

[0039] Next, among the perpendicularly oriented carbon nanotubes 15 constituting the CNT forest f, the carbon nanotubes located at the ends are drawn. FIG. 7 shows a state in which perpendicularly oriented carbon nanotubes are drawn using a member P for drawing carbon nanotubes. For ease of description, FIG. 7 shows an enlarged view of the member P and the CNT forest f. As the member P, tweezers or the like can be used. By drawing the carbon nanotubes located at the ends of the CNT forest f, the carbon nanotubes adjacent to the drawn carbon nanotubes are successively drawn due to van der Waals forces, and the unidirectionally oriented film 10W is formed in which the carbon nanotubes located at the ends are oriented in the direction in which they are drawn. The plurality of drawn carbon nanotubes that constitute the carbon nanotube fiber 10 are bonded to one another by van der Waals bonding. FIG. 7 is a cross-sectional view, and does not show a state in the depth direction (y direction) of the page, but the CNT forest f also spreads in the depth direction of the page. Since van der Waals forces are applied to the carbon nanotubes 15 in the CNT forest f, the carbon nanotube 15 is drawn at a certain position in the y direction so that the carbon nanotubes 15 located in the $\pm y$ direction relative to the drawn carbon nanotube 15 are also drawn. In the case of forming the unidirectionally oriented film 10W that spreads in the depth direction of the page in FIG. 7, it is easy to obtain the unidirectionally oriented film that spreads in the depth direction of the page, for example, by using the member P that spreads in the depth direction of the page. Further, the unidirectionally oriented film 10W may be formed by winding the film up using a winding drum that extends in the depth direction of the page.

[0040] The thickness of the unidirectionally oriented film 10W is, for example, about 140 nm, but may be larger or smaller than this thickness. When the unidirectionally oriented film 10W having a large thickness is used, the diameter of the obtained continuous conjugate fibers is large, and when the unidirectionally oriented film 10W having a small thickness is used, the diameter of the obtained continuous conjugate fibers is small.

[0041] FIG. 6 is a perspective view showing an example of a configuration of a device that uses an adding step of the continuous conjugate fiber production method according to an embodiment of the present invention. A device 200 shown in FIG. 6 is a device for performing an adding step by a dry method, and is a typical example of an adding unit. The device 200 includes, for example, a housing 30 in which a first support member 31, a second support member 32, and fans 51 and 52 are formed. For ease of description, FIG. 6 shows a state in which the inside of the housing 30 is visible and is indicated by a two-dot chain line. The first support member 31 and the second support member 32 are provided in parallel at, for example, the end of the housing 30 in the z direction. The housing 30 is formed, for example, so that the inside is a closed space. The unidirectionally oriented film 10W is

supported by the first support member 31 and the second support member 32. The first support member 31 and the second support member 32 are formed to be detachable from the housing 30. The first support member 31 and the second support member 32 may be configured to be able to unwind and wind the unidirectionally oriented film 10W.

[0042] Since the first support member 31 and the second support member 32 are configured to be able to unwind and wind the unidirectionally oriented film 10W, the orientation of the fibrous material 20 added in the adding step described later is improved. That is, the first support member 31 and the second support member 32 are rotated in the same direction, and the unidirectionally oriented film 10W is unwound from one of the first support member 31 and the second support member 32 and wound up from the other, so that the orientation of the fibrous material 20 is adjusted to be along the orientation direction of the unidirectionally oriented film 10W. In this way, since the orientation of the fibrous material 20 is adjusted by unwinding and winding, in the continuous conjugate fiber production method according to this embodiment, it is preferable to perform the process while unwinding the unidirectionally oriented film 10W.

[0043] In the device 200, for example, a net 40 is installed between the fans 51 and 52 and the first and second support members 31 and 32. In the adding step, when the plurality of fibrous materials 20 are disposed on the net 40, and air currents are generated in the closed space using the fans 51 and 52, the plurality of fibrous materials 20 can be added onto the plurality of carbon nanotube fibers 10 by the air currents. The plurality of fibrous materials 20 are, for example, added to the bottom surface as well as the top surface of the plurality of carbon nanotube fibers 10.

[0044] In the adding step, the mass ratio of the plurality of fibrous materials relative to the plurality of carbon nanotube fibers 10 is, for example, 0.004 or more and 100 or less, preferably 0.71 or more and 40 or less, and may be 0.71 or more and 20 or less.

[0045] Next, the carbon nanotube fibers 10 having the plurality of fibrous materials 20 added thereto are bundled together to form a fibrous continuous conjugate fiber (forming step). For example, some of the carbon nanotube fibers contained in the unidirectionally oriented film 10W having the plurality of fibrous materials 20 added thereto are selected and bundled to form a continuous conjugate fiber.

[0046] In the forming step, when the plurality of carbon nanotube fibers 10 are bundled, the orientation of the fibrous material 20 added to the plurality of carbon nanotube fibers 10 is improved.

[0047] Furthermore, it is preferable to have a twisting step of twisting the continuous conjugate fibers after the forming step. FIG. 8 shows a state in which the unidirectionally oriented film 10W comprises the plurality of carbon nanotube fibers 10 having the plurality of fibrous materials 20 added thereto by an adding unit 301 of a production device 300A, a state in which a plurality of

carbon nanotube fibers having a plurality of fibrous materials added thereto are bundled by a forming unit 302, and a state in which continuous conjugate fibers are twisted by a twisting unit 303. The adding unit 301 of FIG. 8 corresponds to the device 200 of FIG. 6. By twisting the continuous conjugate fibers together, continuous conjugate fibers 101 and 102 are formed in which the plurality of carbon nanotube fibers 10 are formed in a spiral shape around the outer periphery of the plurality of fibrous materials 20 as shown in FIGS. 2 and 3. The continuous conjugate fibers 101 and 102 can be produced by, for example, adjusting the amount of the fibrous material 20 added to the plurality of carbon nanotube fibers 10 by the adding unit 301 in the adding step and the strength with which the carbon nanotube fibers 10 are twisted together by the twisting unit 303 in the twisting step. For example, the adjustment can be performed by one or both of the method of decreasing the amount of the fibrous material 20 added to the plurality of carbon nanotube fibers 10 by the adding unit 301 in the adding step and the method of increasing the twisting strength of the carbon nanotube fiber 10 by the twisting unit 303 in the twisting step.

[0048] In the continuous conjugate fiber 101 in which the plurality of carbon nanotube fibers 10 are formed in a spiral shape around the outer periphery of the plurality of fibrous materials 20, when a force is applied to the fibrous material 20, the stress is transmitted to other fibrous materials 20 and the like through the spiral carbon nanotube fiber 10 that is in contact with the fibrous material 20, and thus the continuous conjugate fiber 101 as a whole exhibits high tensile strength and is less likely to break. Further, in the continuous conjugate fiber 101, since the enclosed fibrous material 20 is less likely to protrude outward, structural stability can be improved.

[0049] Furthermore, the forming step and the twisting step may be performed consecutively. That is, in the forming step, a plurality of carbon nanotube fibers having the plurality of fibrous materials 20 added thereto may be bundled, and the plurality of carbon nanotube fibers 10 having the plurality of bundled fibrous materials 20 added thereto may be twisted together. Even when the plurality of carbon nanotube fibers 10 having the plurality of fibrous materials 20 added thereto are twisted together in the forming step, a continuous conjugate fiber can be formed in which the plurality of carbon nanotube fibers 10 are formed in a spiral shape around the outer periphery of the plurality of fibrous materials 20.

[0050] According to the fibrous material of this embodiment, the continuous conjugate fiber according to the above-described embodiment can be formed by including the adding step of adding the plurality of fibrous materials 20 to the plurality of carbon nanotube fibers 10 and the forming step of bundling the plurality of carbon nanotube fibers 10 having the plurality of fibrous materials 20 added thereto to form a fibrous continuous conjugate fiber. The continuous conjugate fiber according to the above-described embodiment can use the fibrous

materials 20 such as recycled carbon fibers in the form of fibers, and can have a structure with high tensile strength by including the plurality of fibrous materials 20 and the plurality of carbon nanotube fibers 10 arranged to surround the plurality of fibrous materials 20. In the continuous conjugate fiber according to the above-described embodiment, since the plurality of carbon nanotube fibers 10 are formed surrounding the plurality of fibrous materials 20, a force is easily transmitted in the longitudinal direction. Therefore, it is possible to reuse fiber wastes such as prepregs and carbon fibers regardless of their length, which reduces underground pollution caused by landfill disposal and achieves high tensile strength.

[0051] FIG. 9 is a conceptual diagram illustrating another aspect of the adding step in the continuous conjugate fiber production method according to an embodiment of the present invention, which is different from that shown in FIG. 6. A device 201 shown in FIG. 9 has an inlet 33 provided on a side wall of a housing 30A so as to be capable of communicating with the outside. For ease of description, in FIG. 9, the direction in which the fibrous material 20 is introduced from the inlet 33 is indicated by an arrow. The device 201 corresponds to the adding unit 301 of FIG. 8. The device 201 includes a pair of guide members 61 and 62 arranged side by side with a gap therebetween along the longitudinal direction of the plurality of carbon nanotube fibers 10. The pair of guide members 61 and 62 are, for example, cylindrical members that are rotatably provided, and are controlled so that the rotation directions of the pair of guide members 61 and 62 are the same when the distance between the pair of guide members 61 and 62 is at the closest position. In other words, when the guide member 61 rotates counterclockwise, the guide member 62 is configured to rotate clockwise, which is the opposite direction to the rotation direction of the guide member 61, and when the guide member 61 and the guide member 62 are positioned facing each other, the guide member 61 and the guide member 62 are both configured to rotate downward. In addition, although an example in which only one pair of guide members 61 and 62 is formed is shown in FIG. 9, a plurality of pairs of guide members may be provided in the direction perpendicular to the surface of the unidirectionally oriented film 10W. That is, the pair of guide members 61 and 62 may be stacked on top of each other to form a multi-stage structure. When the plurality of pairs of guide members 61 and 62 are provided in the direction perpendicular to the surface of unidirectionally oriented film 10W, for example, the fibrous material is introduced from above the uppermost guide member.

[0052] In the adding step, it is preferable that the plurality of guide members arranged side by side with gaps therebetween along the longitudinal direction of the plurality of carbon nanotube fibers 10 are arranged above the plurality of carbon nanotube fibers arranged in a two-dimensional manner, and the plurality of fibrous materials 20 are placed on the plurality of carbon nanotube fibers

10 through the gaps between the plurality of guide members. By performing the adding step using the above-described method, the orientation of the fibrous material 20 can be controlled in the direction of the gaps between the plurality of guide members, and the fibrous material 20 with high orientation in the longitudinal direction of the plurality of carbon nanotube fibers 10 can be added onto the plurality of carbon nanotube fibers 10.

[0053] In the above-described embodiment, although an example in which the adding step is performed by a dry method has been shown, the adding step may also be performed by a wet method. FIG. 10 is a conceptual diagram illustrating another aspect of the adding step in the continuous conjugate fiber production method according to an embodiment of the present invention, which is different from that shown in FIG. 6. A device 202 shown in FIG. 10 is a device used when the adding step is performed by a wet method. The device 202 corresponds to the adding unit 301 in FIG. 8. The device 202 includes, for example, a housing 30B capable of storing a dispersion liquid L.

[0054] In the adding step, a dispersion liquid L in which the plurality of fibrous materials 20 are dispersed may be prepared, and the plurality of carbon nanotube fibers 10 may be immersed in the dispersion liquid L to add the fibrous materials 20 to the plurality of carbon nanotube fibers 10. The dispersoid of the dispersion liquid L is the fibrous material 20. The dispersion medium of the dispersion liquid L is water, ethanol, NMP (N-methyl-2-pyrrolidone), or the like. When the adding step is performed by a wet method, for example, the carbon nanotube fibers 10 are immersed in the dispersion liquid L in the device 202, and then the plurality of carbon nanotube fibers 10 are dried. The plurality of carbon nanotube fibers 10 may be dried either in a room temperature environment or in a high temperature environment. In the adding step according to a wet method, it is preferable to use the plurality of carbon nanotube fibers 10 in the form of the unidirectionally oriented film 10W.

[0055] Further, after the forming step or the twisting step, another step may be further included. For example, a pre-forming step of wrapping the fibrous continuous conjugate fiber formed after the forming step or the twisting step with a plurality of carbon nanotube fibers may be further included. FIGS. 11 and 12 are conceptual diagrams of modified examples of the continuous conjugate fiber production method according to an embodiment of the present invention and illustrating the pre-forming step. A production device 300B shown in FIG. 11 includes a pre-forming unit 304 in addition to the adding unit 301, the forming unit 302, and the twisting unit 303.

[0056] In the pre-forming step, for example, the pre-forming unit 304 wraps the fibrous continuous conjugate fibers 100 and 101 with at least one unidirectionally oriented film 10W. Although FIG. 12 shows an example in which only one unidirectionally oriented film 10W is used, the plurality of unidirectionally oriented films 10W may be used. By wrapping the fibrous continuous con-

jugate fibers 100 and 101 in the unidirectionally oriented film 10W, the continuous conjugate fibers are configured such that multiple layers composed of carbon nanotube fibers are formed on the radially outer side of the fibrous material.

[0057] Further, in the forming step, the plurality of carbon nanotube fibers having a plurality of fibrous materials added thereto may be bundled together with the plurality of carbon nanotube fibers having no fibrous material added thereto to form a fibrous continuous conjugate fiber. FIG. 13 is a conceptual diagram of another modified example of the forming step of the continuous conjugate fiber production method according to an embodiment of the present invention.

[0058] In the forming step, when the plurality of carbon nanotube fibers having a plurality of fibrous materials added thereto are bundled together with the plurality of carbon nanotube fibers having no fibrous material added thereto to form a fibrous continuous conjugate fiber, as shown in FIG. 13, the unidirectionally oriented film 10W having the fibrous material 20 added thereto may be stacked and bundled with at least one unidirectionally oriented film 10W having no fibrous material 20 added thereto. The unidirectionally oriented film having no fibrous material 20 added thereto is, for example, overlapped from at least one side in the perpendicular direction of the unidirectionally oriented film 10W having the fibrous material 20 added thereto, and may be overlapped from both sides. The continuous conjugate fibers formed by bundling are, for example, twisted together in the twisting step. In this way, since the contact area between the fibrous material 20 and the plurality of carbon nanotube fibers 10 is increased by stacking and bundling the unidirectionally oriented film 10W having the fibrous material 20 added thereto with at least one unidirectionally oriented film 10W having no fibrous material 20 added thereto, the tensile strength is improved.

[0059] In the forming step, since a fibrous continuous conjugate fiber is formed by bundling the plurality of carbon nanotube fibers 10 having the plurality of fibrous materials 20 added thereto together with the plurality of carbon nanotube fibers 10 having no fibrous material 20 added thereto, multiple layers of the carbon nanotube fiber 10 are formed on the radially outer side of the fibrous material 20. Through the above steps, the diameter of the continuous conjugate fiber becomes larger, and the volume ratio of the carbon nanotube fibers 10 in the continuous conjugate fiber increases.

[0060] According to the continuous conjugate fiber of this embodiment, since the fibrous material 20 such as discontinuous recycled carbon fiber for a mat material is used and the fibrous material 20 is arranged to be surrounded by the plurality of carbon nanotube fibers 10, a continuous fiber or a long fiber can be obtained. Further, in the continuous conjugate fiber of this embodiment, since the plurality of fibrous materials 20 are arranged to be surrounded by the plurality of carbon nanotube fibers 10, there is a high degree of freedom in the dia-

meter. For example, the fiber can have a diameter of, for example, 10 μm or less or a diameter of 100 μm or more. The diameter of the continuous conjugate fiber is related to the aspect ratio of the continuous conjugate fiber, and affects the physical properties of the continuous conjugate fiber, such as tensile strength, elastic modulus, and breaking strain.

[0061] Although the embodiment of the present invention has been described in detail above, the present invention is not limited to the above-described embodiment, and various omissions, substitutions, modifications, and changes are possible within the scope of the gist of the present invention described in the claims. These embodiments and their modifications are included in the scope of the invention and its equivalents as described in the claims, as well as in the scope and gist of the invention.

[0062] The upper and/or lower limits of the numerical ranges described in this specification can be arbitrarily combined to define a preferred range. For example, the upper and lower limits of a numerical range can be arbitrarily combined to define a preferred range, the upper limits of a numerical range can be arbitrarily combined to define a preferred range, and the lower limits of a numerical range can be arbitrarily combined to define a preferred range.

[0063] Throughout this disclosure, the singular expressions should be understood to include the plural concept unless otherwise specified. Therefore, singular articles (for example, in the English language, "a," "an," "the," etc.) should be understood to also include the plural concept unless otherwise specified.

[Examples]

[0064] Hereinafter, examples of the present invention will be described. The present invention is not limited to the following examples.

[Example 1]

[0065] First, a silicon substrate with a catalyst thickness of 2 to 50 nm for growing carbon nanotubes was prepared. Next, perpendicularly oriented carbon nanotubes were grown from the catalyst by chemical vapor deposition to prepare perpendicularly oriented carbon nanotubes that were oriented perpendicular to the substrate.

[0066] Next, from the perpendicularly oriented carbon nanotube forest formed on the substrate, one located at an end in one direction was picked up and pulled out so that a plurality of carbon nanotube fibers were arranged in parallel. In this way, a unidirectionally oriented film having a width of 3 to 5 μm and a thickness of 5 to 20 nm was prepared, in which a plurality of carbon nanotube fibers having a diameter of 17 nm were arranged in parallel.

[0067] Next, a device as shown in FIG. 8 was prepared, and a device as shown in FIG. 6 was prepared as a device

corresponding to the adding unit in FIG. 8. In addition, a plurality of recycled carbon fibers were placed on a net (aluminum, glass fiber, plastic mesh). As the recycled carbon fibers, fiber wastes with a length of 1 to 15 mm, from which the resin had been removed and which were composed of carbon, were prepared. Using a scanning electron microscope (manufactured by JEOL, model number: JSM-IT100), the diameter of the recycled carbon fiber was calculated from the average of the average diameters at five points on each of the five recycled carbon fibers, and was found to be 7 μm . Next, the inside of the housing of the device was made into a closed space in a state where the plurality of carbon nanotube fibers were supported by the first support member and the second support member of the device as shown in FIG. 6.

[0068] Next, an airflow was generated in the closed space using a blower, and the plurality of recycled carbon fibers were added to the plurality of carbon nanotube fibers by the airflow.

[0069] Next, the plurality of carbon nanotube fibers having the plurality of recycled carbon fibers added thereto were bundled to form continuous conjugate fibers, which were then twisted together to produce a fibrous continuous conjugate fiber having a length of 45 cm according to Example 1. In Example 1, a plurality of continuous conjugate fibers were produced under similar conditions.

[Example 2]

[0070] The continuous conjugate fibers of Example 1 were further subjected to a pre-forming step. Specifically, after the twisting step, two unidirectionally oriented films similar to the unidirectionally oriented film used in the previous adding step were prepared, and the continuous conjugate fiber produced in the twisting step was wrapped in the unidirectionally oriented films to produce a fibrous continuous conjugate fiber. That is, in Example 2, recycled carbon fiber was wrapped in three layers of the unidirectionally oriented film. The other conditions were the same as in Example 1.

[Comparative Example 1]

[0071] A fibrous material consists of carbon nanotube fibers was produced in the same manner as in Example 1 except that no recycled carbon fibers were used and the adding step was omitted. That is, in Comparative Example 1, a unidirectionally oriented film having a width of 3 to 5 μm and a thickness of 5 to 20 nm was first prepared, in which a plurality of carbon nanotube fibers having a diameter of 17 nm were arranged in parallel. Next, the unidirectionally oriented films which consist of the plurality of carbon nanotube fibers were bundled to form continuous fibers and then twisted together to produce a fibrous material having a length of 45 cm.

[Structural evaluation]

[0072] First, the continuous conjugate fibers of Examples 1 and 2 and the fibrous material of Comparative Example 1 were observed with a scanning electron microscope. FIG. 14 is an SEM image of the continuous conjugate fiber of Example 1, FIG. 15 is an SEM image of the continuous conjugate fiber of Example 2, and FIG. 16 is an SEM image of the fibrous material of Comparative Example 1. In Examples 1 and 2, the continuous conjugate fiber consists of recycled carbon fibers arranged in a row.

[0073] Further, in the SEM images of Example 1, Example 2, and Comparative Example 1, the diameters were measured at five points in the image range, and the average was calculated to calculate the average diameter. FIGS. 14 to 16 show the diameters measured in the respective SEM images. In all of the fibrous materials, the diameter was substantially the same in the longitudinal direction regardless of the measurement points in the SEM images confirmed in FIGS. 14 to 16.

[0074] FIGS. 14 to 16 are views of the vicinity of the axial end of each fiber, and FIGS. 14 and 15 show the points where recycled carbon fibers protrude from the unidirectionally oriented film. It is considered that these points were formed when the unidirectionally oriented film was pulled to be twisted in the twisting step.

[0075] Further, FIG. 17 is an SEM image different from FIG. 14, which is an SEM image of the continuous conjugate fiber obtained by increasing the amount of recycled carbon fiber added in the adding step in the continuous conjugate fiber of Example 1 and adjusting the wrapping using the plurality of oriented films in the pre-forming step. In the continuous conjugate fiber of Example 1 shown in FIG. 17, the angle formed by the extension direction C_{20} of the carbon nanotube fibers relative to the longitudinal direction C_{100} of the continuous conjugate fiber was 20°.

[Tensile strength measurement]

[0076] Tensile strength measurements were performed on the continuous conjugate fibers of Examples 1 and 2 and the fibrous material of Comparative Example 1. The tensile strength was measured using a tabletop tensile tester (Tokai Test Instruments Manufacturing Co., Ltd., TMT-1003) according to the method of ISO 11566: 1996.

[0077] FIG. 18 is a graph showing the strength of the continuous conjugate fiber of Example 1. FIG. 19 is a graph showing the strength of the continuous conjugate fiber of Example 2. FIG. 20 is a graph showing the strength of the fibrous material of Comparative Example 1. In each of Example 1, Example 2, and Comparative Example 1, strength measurements were performed on a plurality of samples prepared under similar conditions. Since these examples and comparative examples were performed manually, there may be some variation in

characteristics for experimental data under similar conditions.

[0078] Further, experimental data with high noise and low reliability has been omitted from the graph. In FIG. 18, the vertical axis represents the load applied to the continuous conjugate fiber in the longitudinal direction, and the horizontal axis represents the movement amount of the crosshead.

[0079] Comparing the continuous conjugate fibers of Example 1 and Example 2, it was confirmed that in Example 2, the tensile strength tends to improve by wrapping the recycled carbon fibers with many unidirectionally oriented films.

[Example 3]

[0080] A continuous conjugate fiber was produced in the same manner as in Example 1 except that the size of the continuous conjugate fiber forming the unidirectionally oriented film in the direction perpendicular to the axial direction (width direction) was changed to 5 cm and the amount of recycled carbon fiber added to the unidirectionally oriented film in the addition process was increased. In Example 3, a continuous conjugate fiber was produced in which 16 rows of recycled carbon fibers were arranged in one cross section.

[0081] In Example 3, a total mass of 6.0×10^{-4} g of recycled carbon fiber was added to a unidirectionally oriented film with a total mass of 8.75×10^{-5} g, so that the specific gravity of the recycled carbon fiber relative to the carbon nanotube fiber (recycled carbon fiber/carbon nanotube fiber) was 6.875.

[Example 4]

[0082] A continuous conjugate fiber was produced in the same manner as in Example 3 except that the continuous conjugate fiber produced in Example 3 was subjected to a pre-forming step and that the amount of recycled carbon fiber added to the unidirectionally oriented film in the adding step was increased. In the pre-forming step, after a twisting step, a unidirectionally oriented film similar to the unidirectionally oriented film used in the previous adding step was prepared, and the continuous conjugate fibers formed in the twisting step were wrapped in the unidirectionally oriented film. That is, in Example 4, the recycled carbon fibers were wrapped with two layers of unidirectionally oriented films. In Example 4, a continuous conjugate fiber was produced in which the recycled carbon fibers were arranged in 36 rows in one cross section.

[0083] In Example 4, a total mass of 1.4×10^{-3} g of recycled carbon fiber was added to a unidirectionally oriented film with a total mass of 9.20245×10^{-5} g, so that the specific gravity of the recycled carbon fiber relative to the carbon nanotube fiber (recycled carbon fiber/carbon nanotube fiber) was 15.213.

[0084] FIG. 21 is an SEM image of the continuous

conjugate fiber of Example 4. The average diameter calculated from the diameters at five points in the SEM image was $93.817 \mu\text{m}$.

5 [Tensile strength measurement]

[0085] The strength of the continuous conjugate fiber was measured under the same conditions as in Examples 1 and 2 and Comparative Example 1 except that the tensile tester was changed to a tabletop tensile/compression tester (MCT-2150W, manufactured by A&D Co., Ltd.). FIG. 22 is a graph showing the strength of the continuous conjugate fiber of Example 3. FIG. 23 is a graph showing the strength of the continuous conjugate fiber of Example 4. In each of Examples 3 and 4, five samples were prepared under similar conditions, and their strengths were measured.

[0086] Comparing FIGS. 22 and 23, it was confirmed that Example 4, which contains a larger amount of recycled carbon fiber and carbon nanotube fiber, exhibited higher strength.

[Example 5]

[0087] A unidirectionally oriented film having a width of 5 mm was prepared, and recycled carbon fibers were added to the unidirectionally oriented film in an adding step. Then, the forming step and the twisting step were performed to form a continuous conjugate fiber in which a plurality of recycled carbon fibers were arranged in a row. Next, a unidirectionally oriented film having a width of 10 mm was prepared, and in a pre-forming step, the continuous conjugate fiber was wrapped in the unidirectionally oriented film to produce the continuous conjugate fiber of Example 5.

[0088] The continuous conjugate fiber of Example 5 was observed with a scanning electron microscope. FIG. 24 is an SEM image of the continuous conjugate fiber of Example 5. In FIG. 24, the recycled carbon fiber rCF is indicated by a drawing line. From FIG. 24, it was confirmed that in Example 5, the recycled carbon fibers enclosed in the carbon nanotube fibers in the continuous conjugate fibers were arranged in a row. In the point shown in FIG. 24, it was confirmed by the SEM image that the recycled carbon fibers were arranged with gaps therebetween. The gaps between the recycled carbon fibers are the bright areas located between the recycled carbon fibers indicated by the symbol "rCF" and the arrows in the SEM image of FIG. 24.

[0089] The strength of the continuous conjugate fiber of Example 5 was measured in the same manner as in Example 1. FIG. 25 is a graph showing the strength of the continuous conjugate fiber of Example 5. In Example 5, ten samples were prepared under similar conditions, and the experimental data for each sample are shown in FIG. 25. In FIG. 25, the horizontal axis represents the ratio of the length of the continuous conjugate fiber before and after the tensile strength measurement, and represents

the ratio of the change in length after the tensile strength test to the length of the continuous conjugate fiber before the tensile strength test.

[Example 6]

[0090] A continuous conjugate fiber which has a length of 30 cm and in which the recycled carbon fiber was surrounded by a plurality of carbon nanotube fibers was produced in the same manner as in Example 1 except that all the recycled carbon fibers used were changed to those having a length of about 6 mm and that a unidirectionally oriented film having a width of about 3 mm was used. That is, the recycled carbon fiber used in Example 6 was made of carbon from which the resin had been removed as in Example 1, and the number of unidirectionally oriented films used in Example 6 was one.

[0091] FIG. 26 is an SEM image of the continuous conjugate fiber of Example 6. The average diameter calculated from the diameters at five points in the SEM image was 9.94 μm .

[0092] The tensile strength of the continuous conjugate fiber of Example 6 was measured in the same manner as in Example 1. FIG. 27 is a graph showing the strength of the continuous conjugate fiber of Example 6. In Example 6, four samples were prepared under similar conditions, and FIG. 27 shows the experimental data for each sample.

[0093] Further, FIG. 28 is a graph showing the correlation between the average diameter obtained by calculating the diameter at five points in each of the four samples produced and subjected to strength measurement in Example 6 and the tensile strength (fiber strength) measured for each sample. FIG. 28 also shows an approximation line of the plotted measurement results of the four samples using the least squares method. The determination coefficient R^2 of the approximation line was 0.77. The average diameter of the four samples is 17.29 μm , and the average tensile strength is 905.68 MPa. Thus, it was confirmed that Example 6 exhibited excellent tensile strength. The variation coefficient CV, calculated by dividing the standard deviation of the tensile strength by the average value of the tensile strength, 905.68 MPa, was 63.80%.

INDUSTRIAL APPLICABILITY

[0094] According to the continuous conjugate fiber of the above-described embodiment, carbon fibers recovered from CFRP and the like can be reused, which can contribute to the problem of recycling CFRP. Further, the continuous conjugate fiber obtained by this embodiment can be made from recycled carbon fibers, which are short fibers, into continuous fibers, and can be reused in automobiles.

REFERENCE SIGNS LIST

[0095]

- 5 10 Carbon nanotube fiber
- 10W Unidirectionally oriented film
- 15 Carbon nanotube
- 20, 20a, 20b, 20c, 20d, 20e, 20f, 20g Fibrous material
- 10 30, 30A, 30B Housing
- 31 First support member
- 32 Second support member
- 33 Inlet
- 40 Net
- 15 51, 52 Fan
- 61, 62 Guide member
- 100, 101, 102 Continuous conjugate fiber
- 200, 201, 202 Device

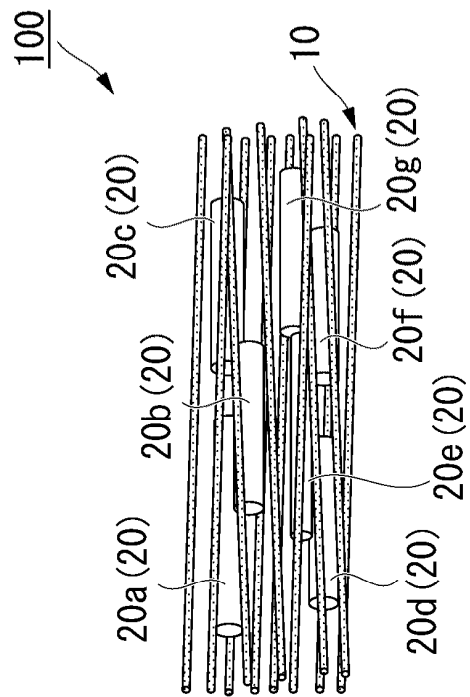
Claims

1. A continuous conjugate fiber comprising:
 - 25 a plurality of fibrous materials; and
 - a plurality of carbon nanotube fibers which are arranged to surround the plurality of fibrous materials.
- 30 2. The continuous conjugate fiber according to claim 1, wherein a tensile strength of a single fibrous material is lower than a tensile strength of a single carbon nanotube fiber constituting the plurality of carbon nanotube fibers.
- 35 3. The continuous conjugate fiber according to claim 1, wherein the fibrous material comprises carbon fibers.
- 40 4. The continuous conjugate fiber according to claim 1,
 - wherein each of the plurality of carbon nanotube fibers comprises a plurality of carbon nanotubes, and
 - 45 wherein the plurality of carbon nanotubes are bonded to each other by van der Waals forces.
5. The continuous conjugate fiber according to claim 1,
 - 50 wherein the fibrous material has a diameter of 5 μm or more and 50 μm or less, and
 - wherein the carbon nanotube fiber has a diameter of 4 nm or more and 50 nm or less.
- 55 6. The continuous conjugate fiber according to claim 1, wherein the plurality of carbon nanotube fibers constitute twisted yarns.

7. A continuous conjugate fiber production device comprising:
- an adding unit which adds a plurality of fibrous materials to a plurality of carbon nanotube fibers; and
- a forming unit which bundles the plurality of carbon nanotube fibers having the plurality of fibrous materials added thereto to form a fibrous continuous conjugate fiber.
8. The continuous conjugate fiber production device according to claim 7, further comprising:
- a twisting unit which twists the continuous conjugate fibers.
9. A continuous conjugate fiber production method comprising:
- an adding step of adding a plurality of fibrous materials to a plurality of carbon nanotube fibers; and
- a forming step of bundling the plurality of carbon nanotube fibers having the plurality of fibrous materials added thereto to form a fibrous continuous conjugate fiber.
10. The continuous conjugate fiber production method according to claim 9,
- wherein in the adding step, the plurality of carbon nanotube fibers are a unidirectionally oriented film.
11. The continuous conjugate fiber production method according to claim 9,
- wherein a strength of a single fibrous material is lower than a strength of a single carbon nanotube fiber constituting the plurality of carbon nanotube fibers.
12. The continuous conjugate fiber production method according to claim 9,
- wherein the fibrous material comprises carbon fiber.
13. The continuous conjugate fiber production method according to claim 9,
- wherein in the adding step, an airflow is generated in a closed space, and the plurality of fibrous materials are added to the plurality of carbon nanotube fibers by the airflow.
14. The continuous conjugate fiber production method according to claim 10,
- wherein in the adding step, the plurality of carbon nanotube fibers are arranged two-dimensionally, and the plurality of fibrous materials are placed on the plurality of carbon nanotube fibers arranged two-dimensionally.
15. The continuous conjugate fiber production method according to claim 9,
- wherein in the adding step, a plurality of guide members arranged with gaps therebetween along a longitudinal direction of the plurality of carbon nanotube fibers are arranged above the plurality of carbon nanotube fibers arranged two-dimensionally, and the plurality of fibrous materials are placed on the plurality of carbon nanotube fibers through the gaps between the plurality of guide members.
16. The continuous conjugate fiber production method according to claim 9,
- wherein in the adding step, a dispersion liquid in which the plurality of fibrous materials are dispersed is prepared, and the plurality of carbon nanotube fibers are immersed in the dispersion liquid to add the plurality of fibrous materials to the plurality of carbon nanotube fibers.
17. The continuous conjugate fiber production method according to claim 9, further comprising:
- a twisting step of twisting the continuous conjugate fibers after the forming step.

FIG. 1

(a)



(b)

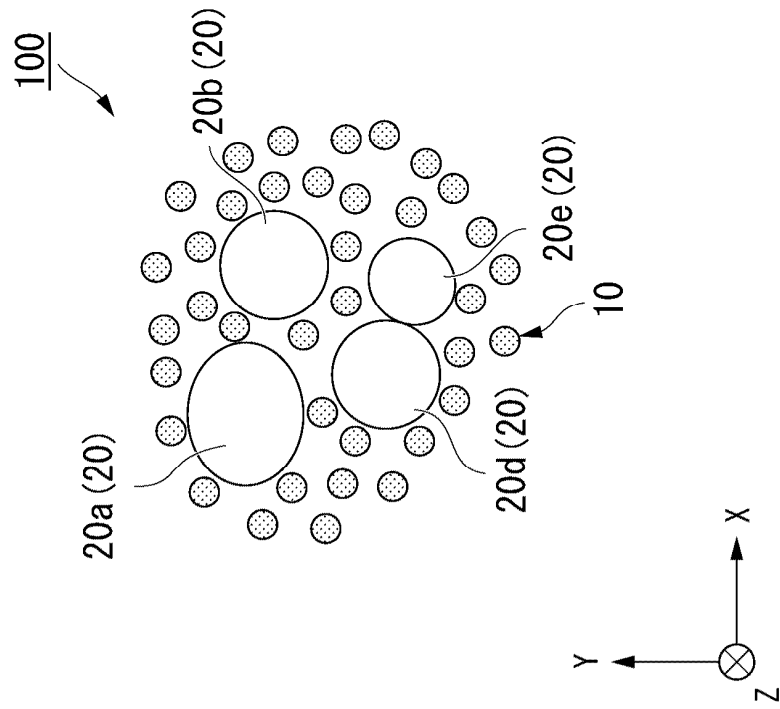


FIG. 2

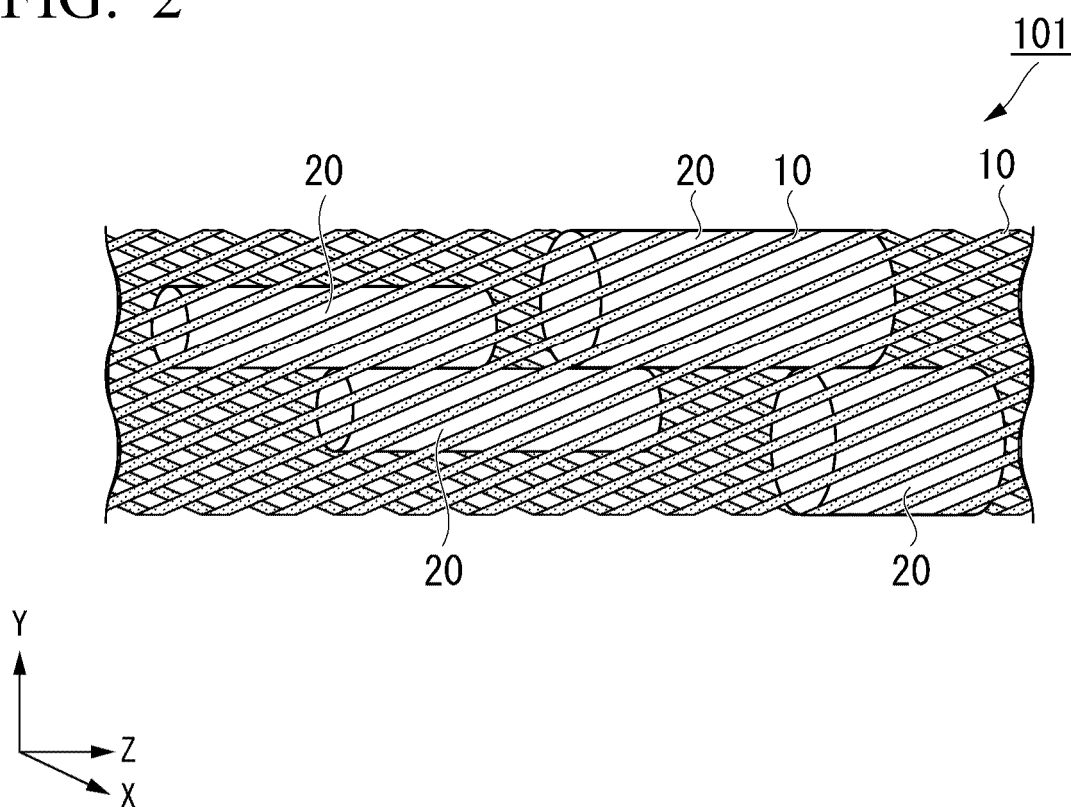


FIG. 3

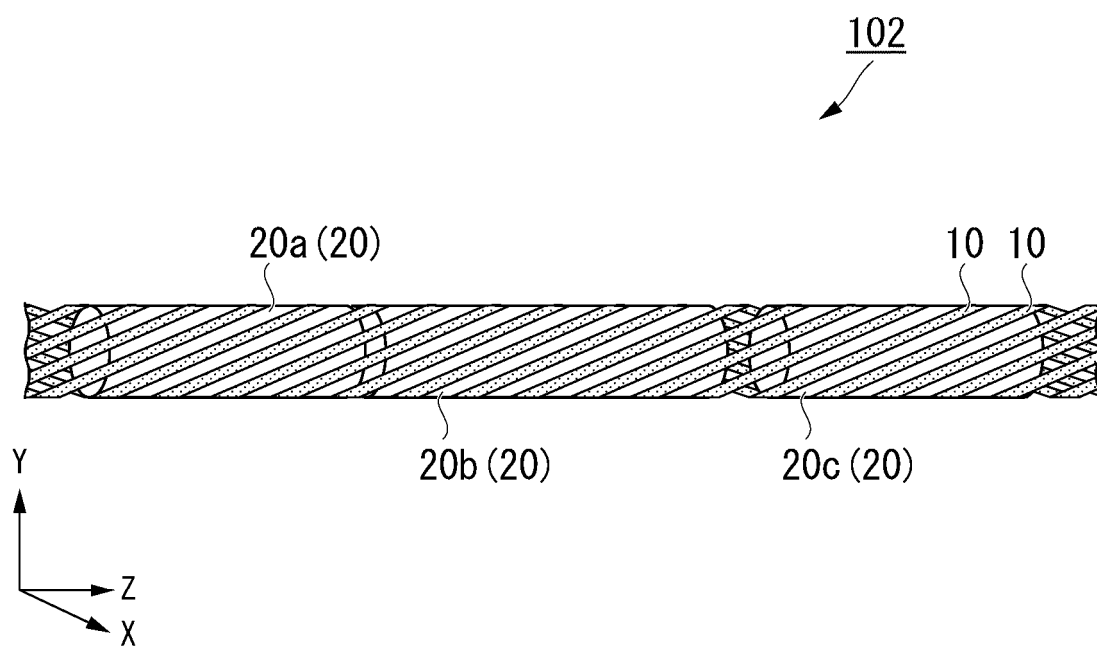


FIG. 4

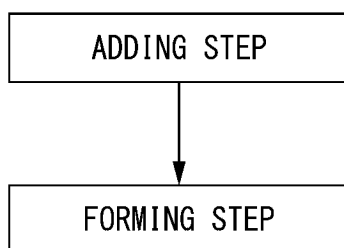


FIG. 5

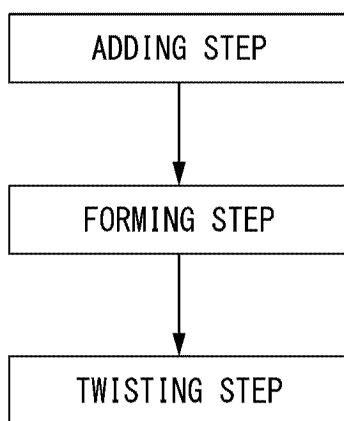


FIG. 6

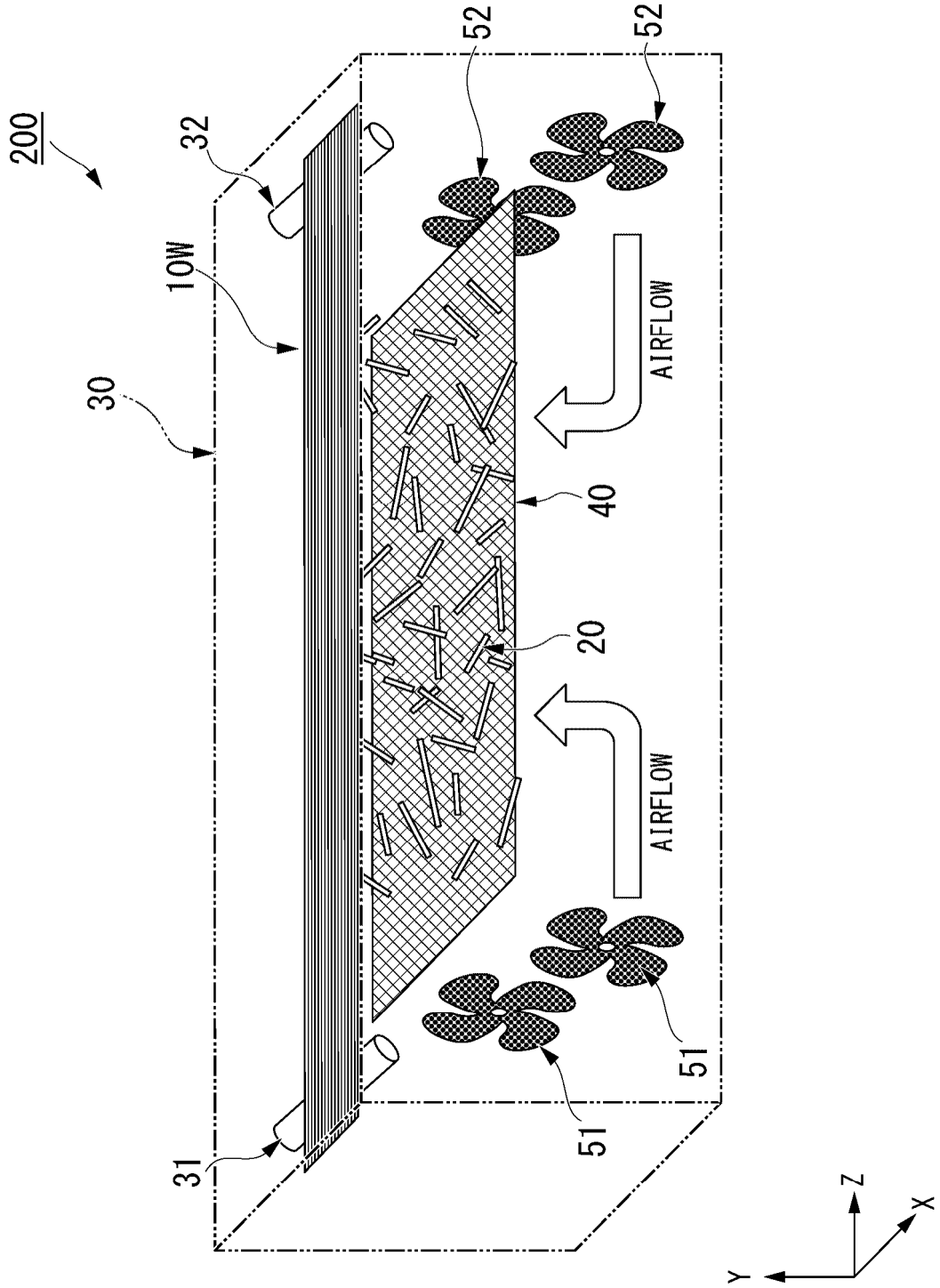


FIG. 7

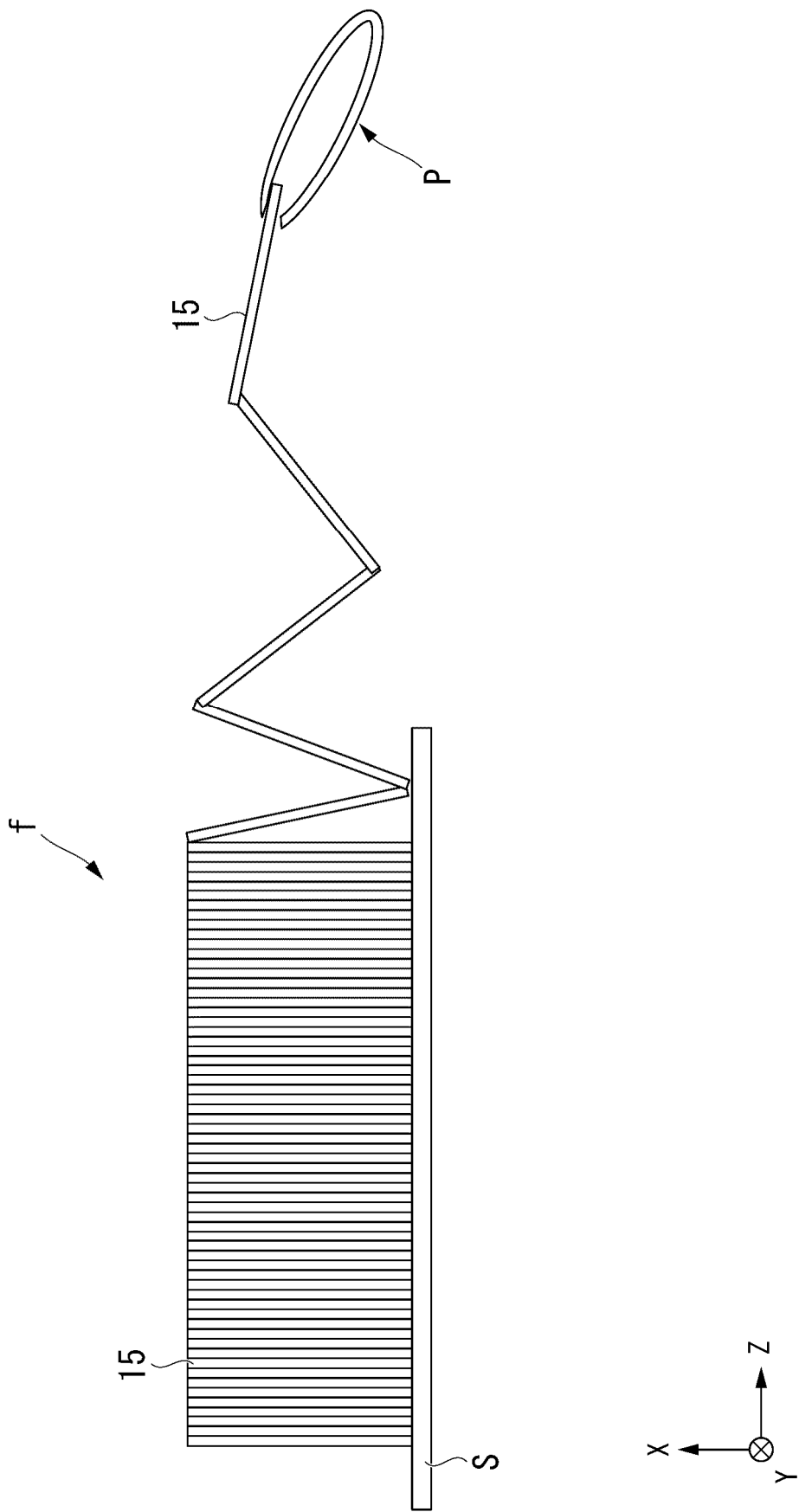


FIG. 8

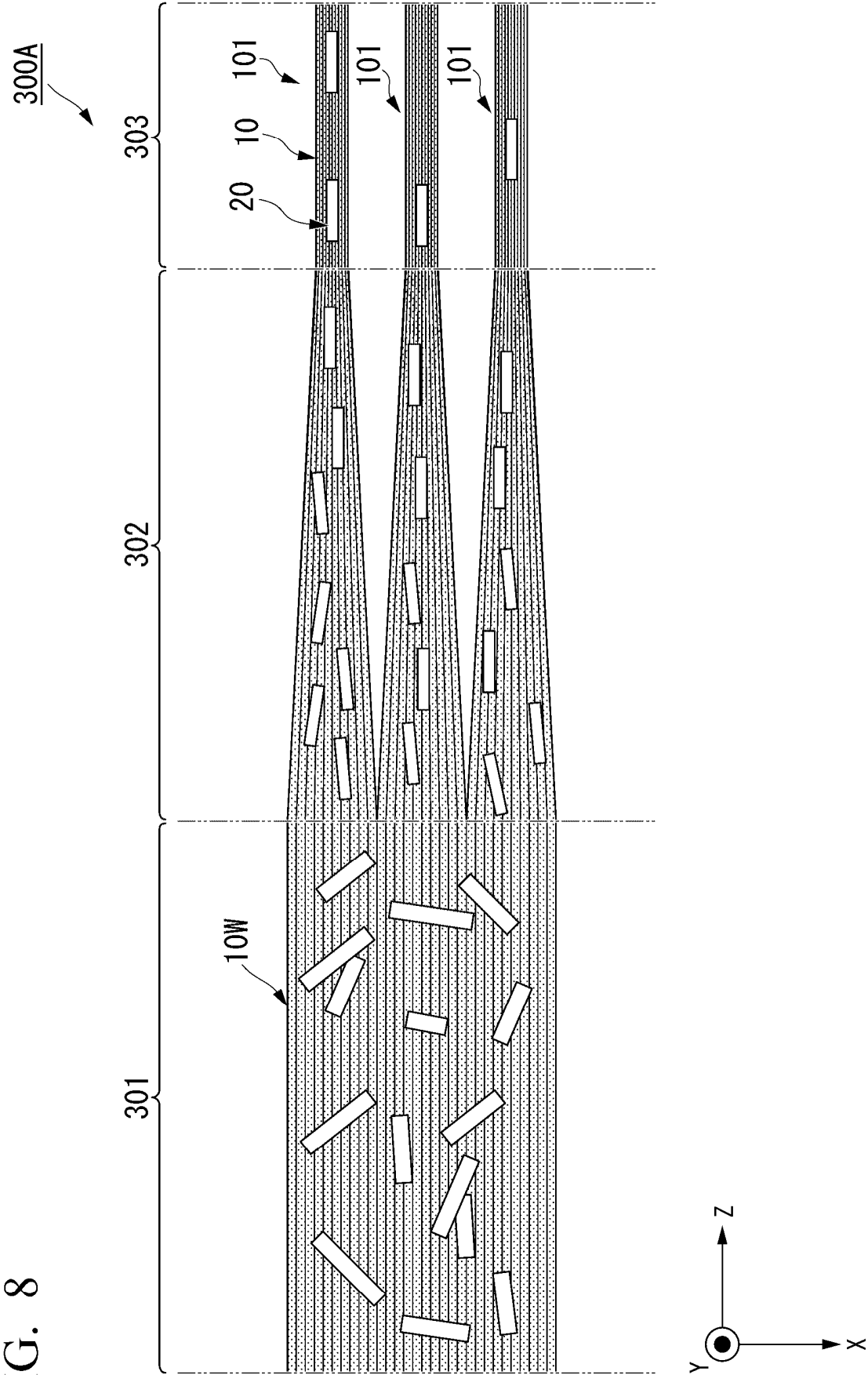


FIG. 9

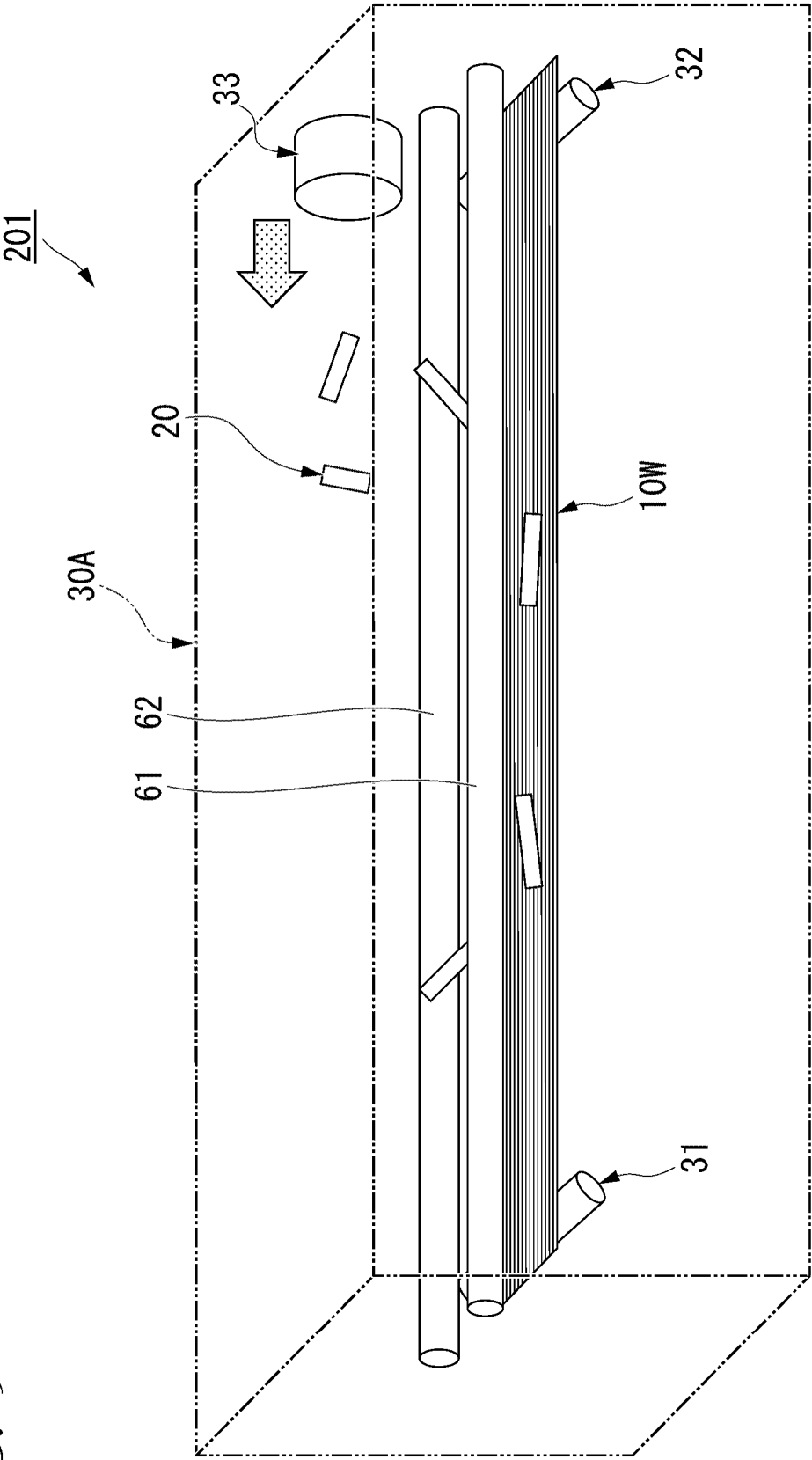


FIG. 10

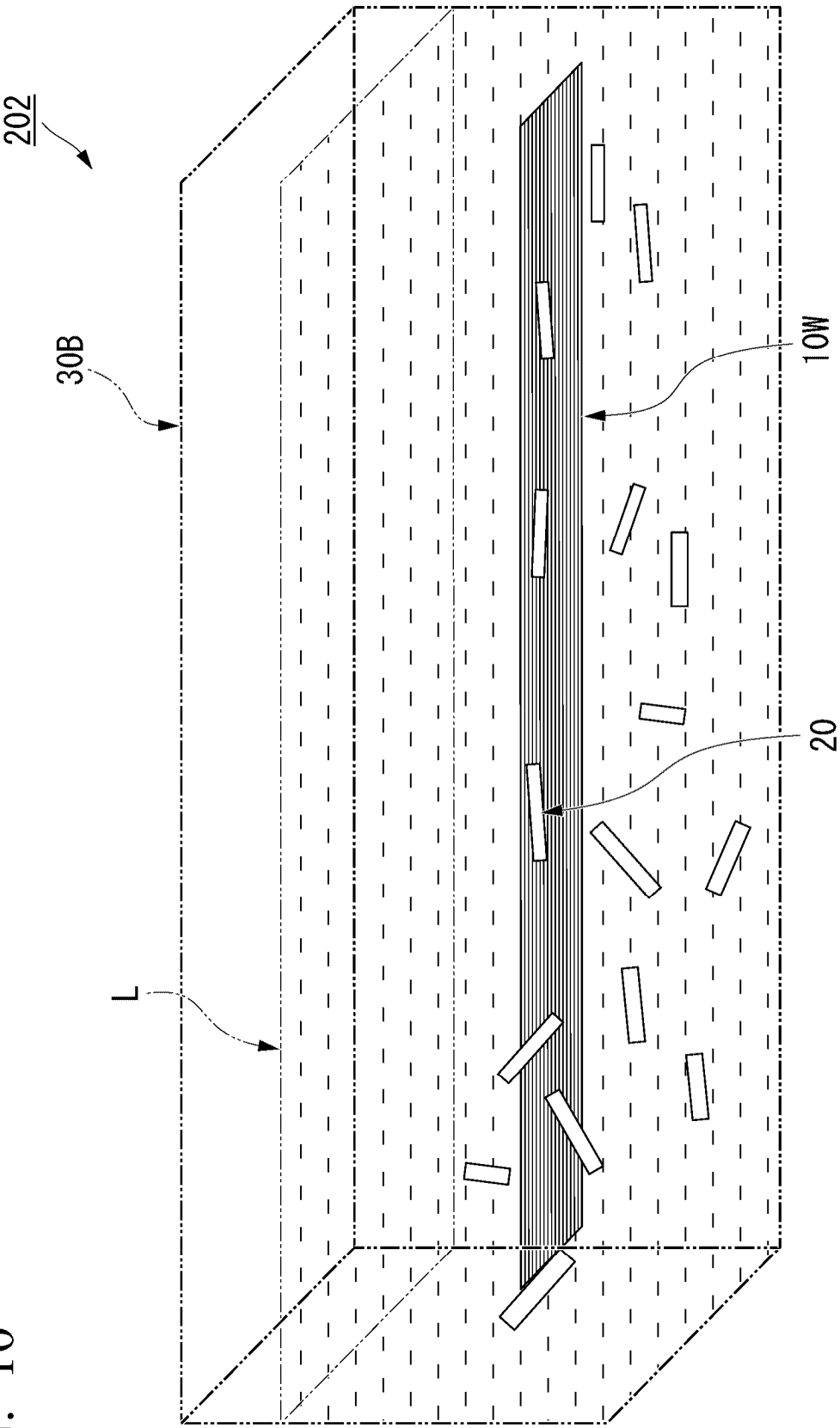


FIG. 11

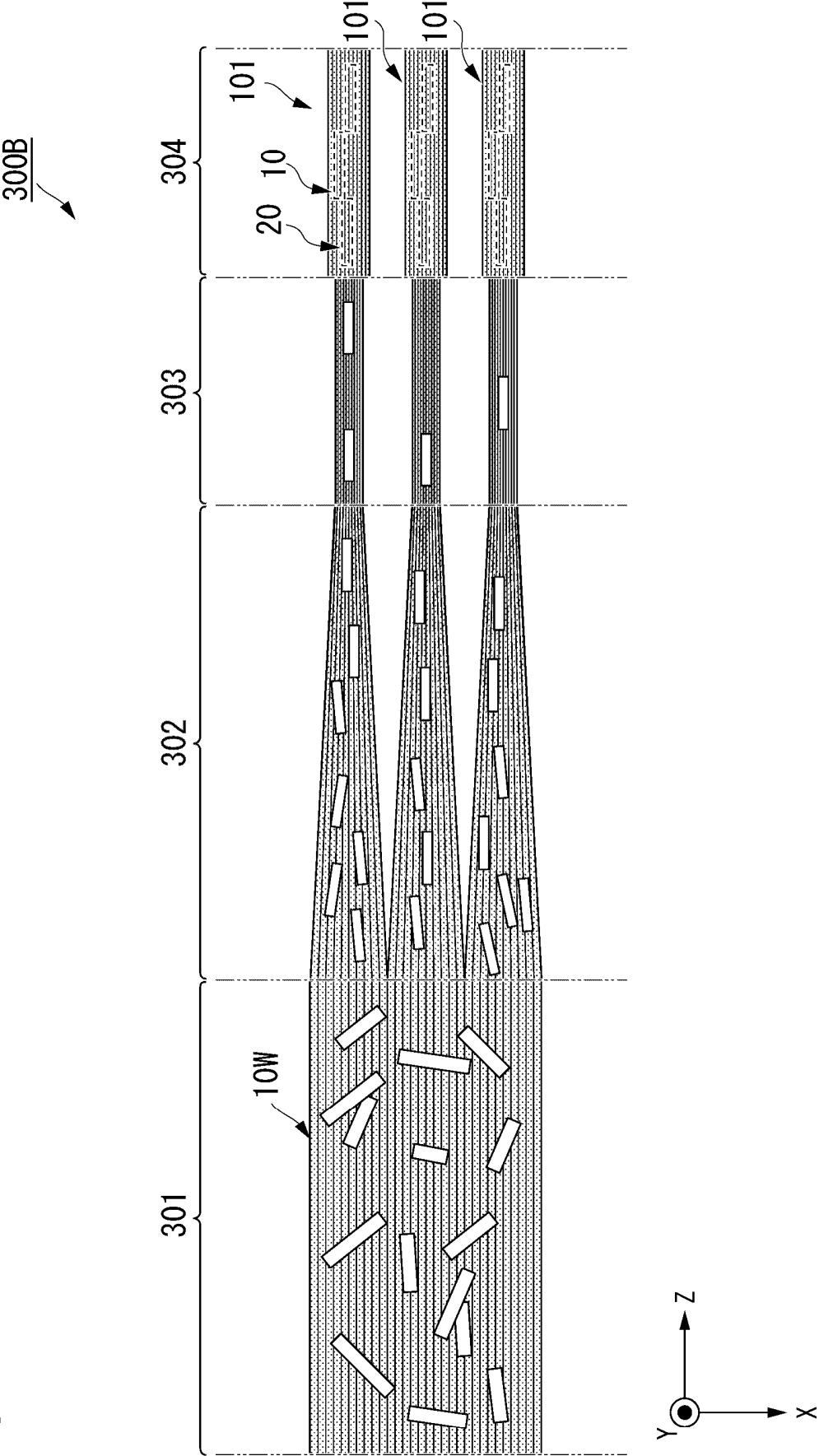


FIG. 12

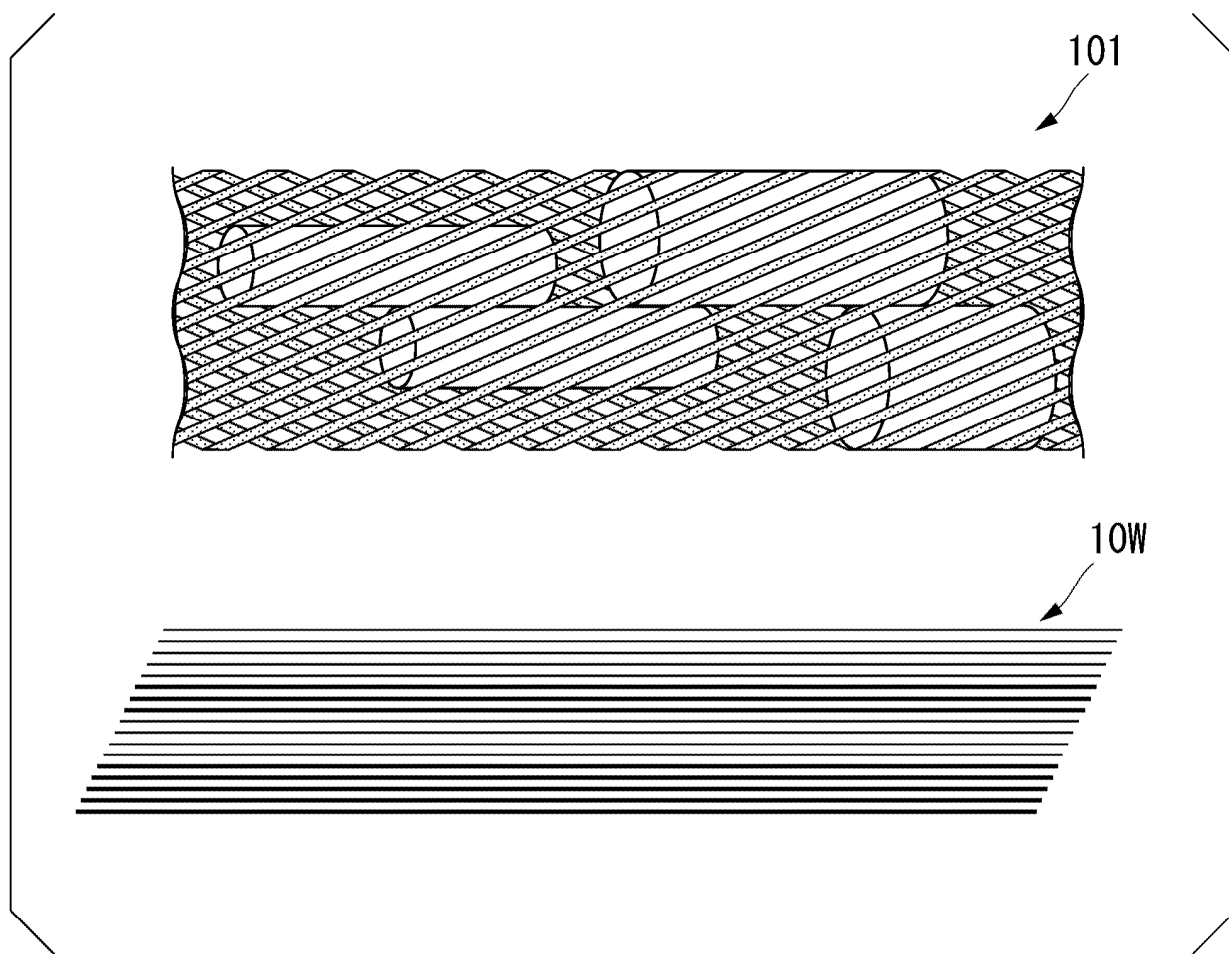


FIG. 13

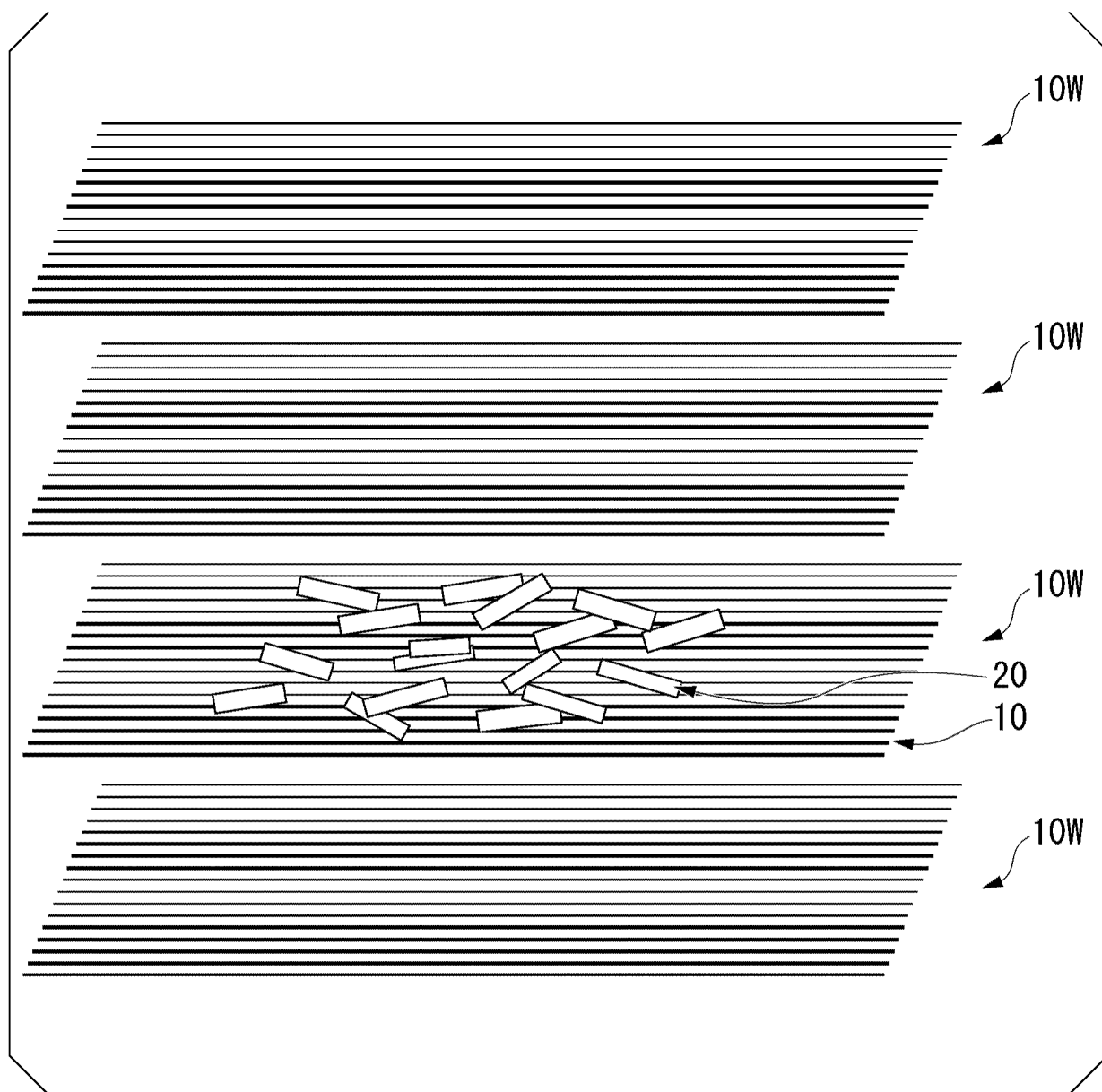


FIG. 14

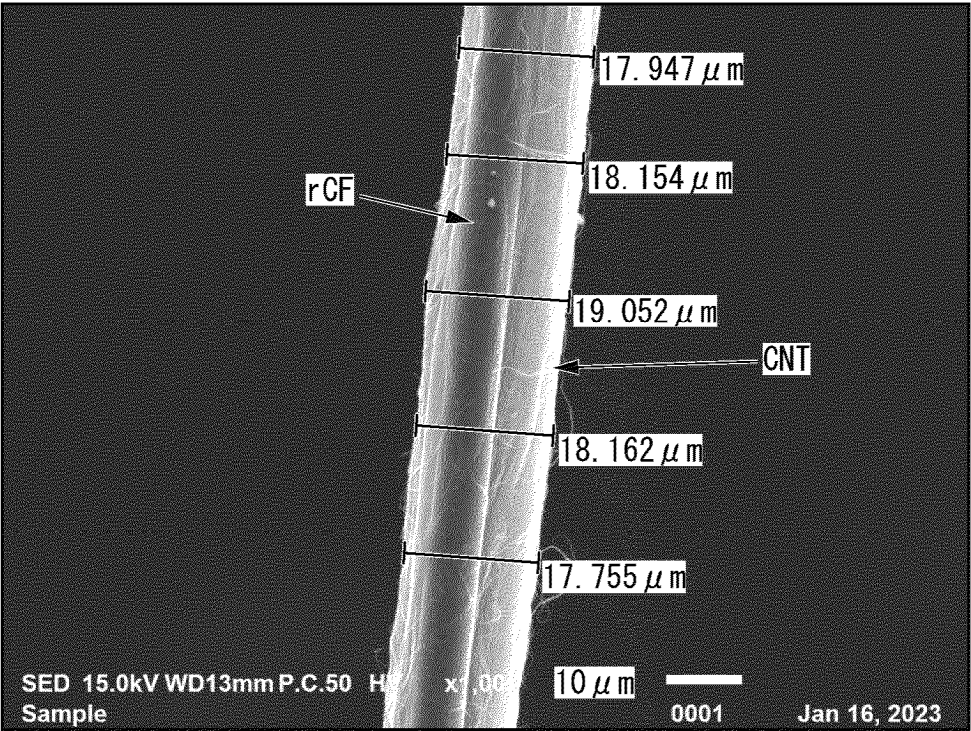


FIG. 15

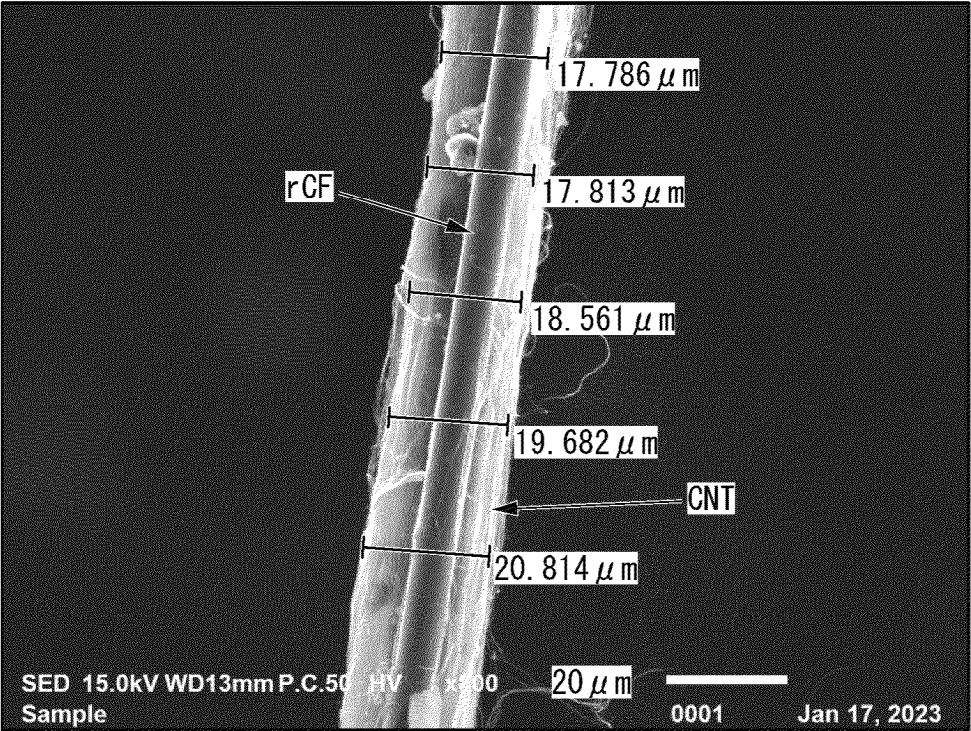


FIG. 16

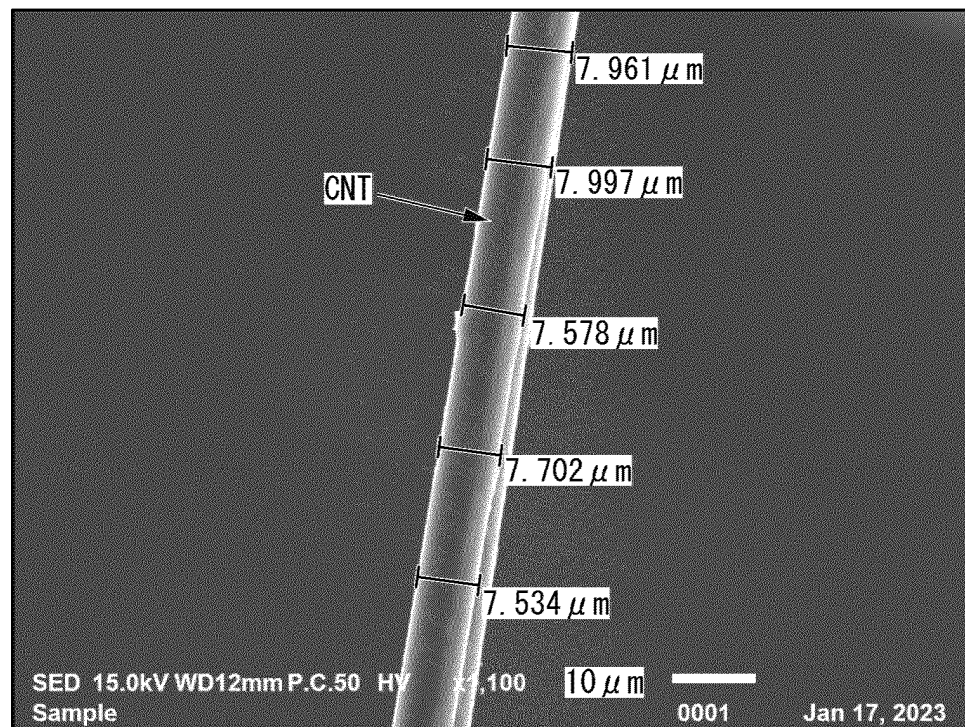


FIG. 17

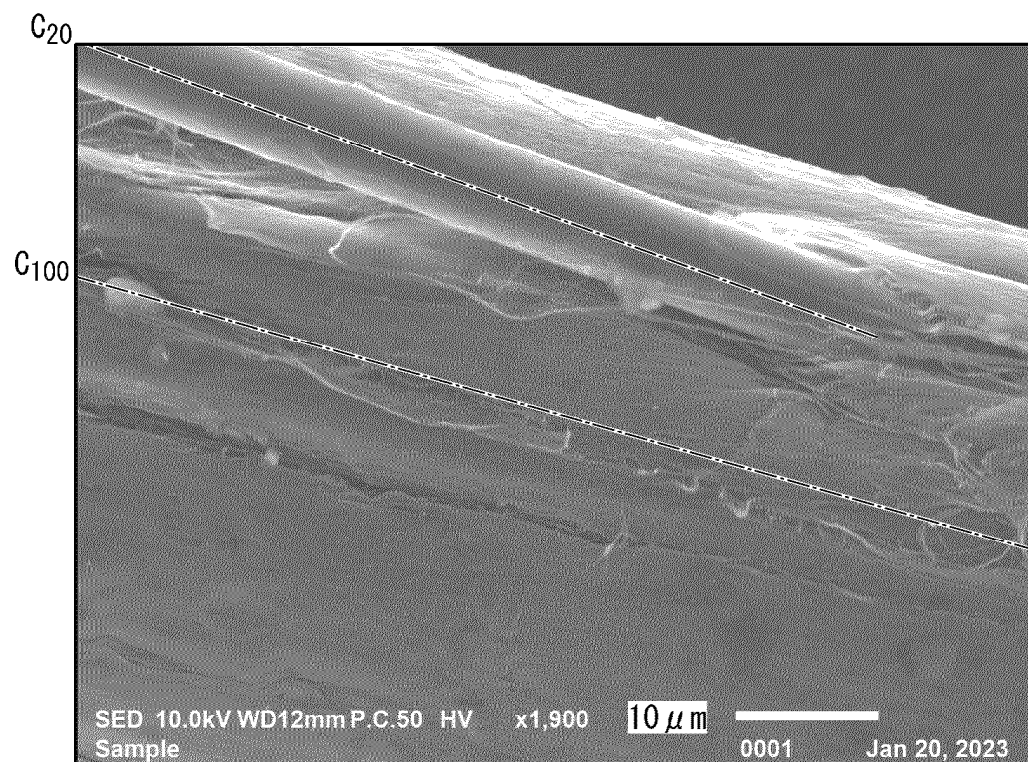


FIG. 18

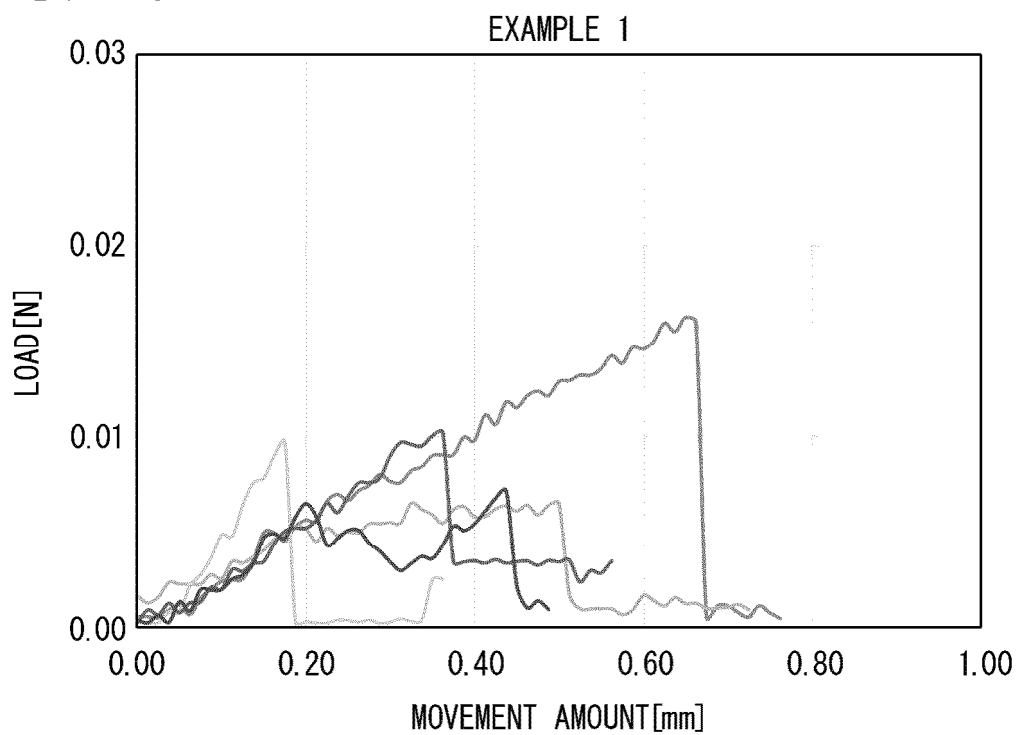


FIG. 19

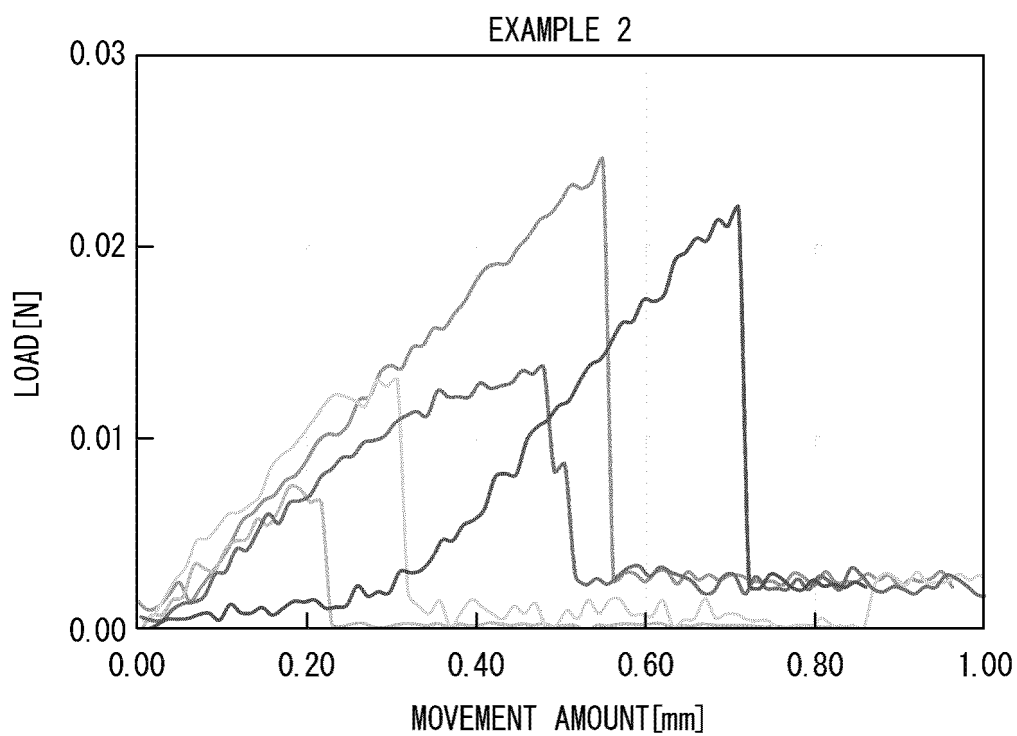


FIG. 20

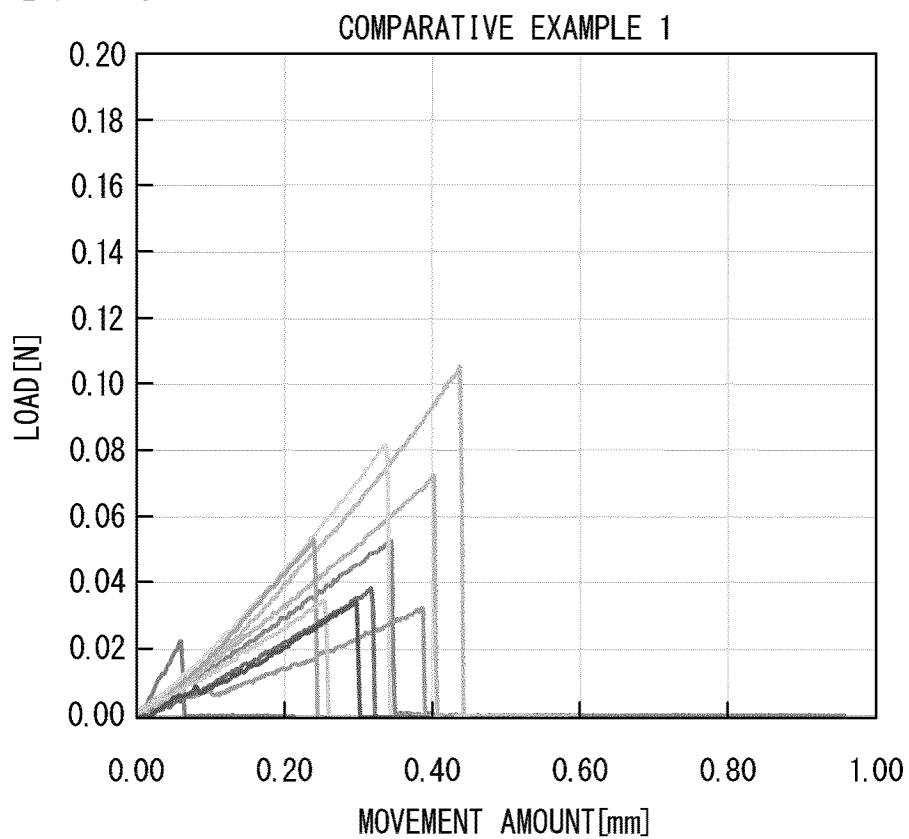


FIG. 21

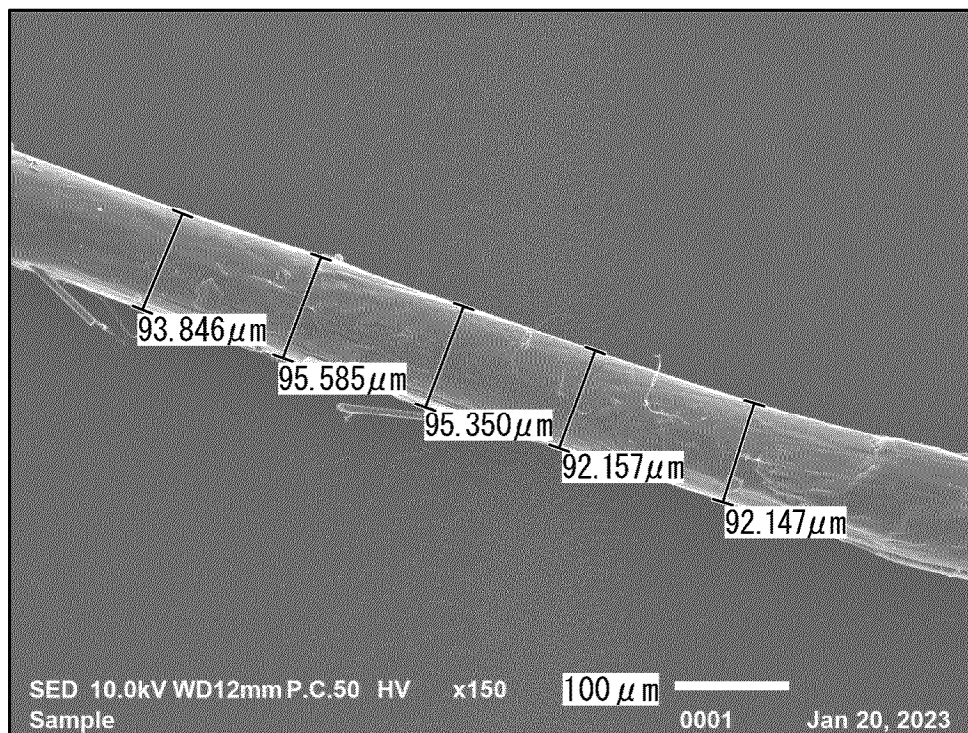


FIG. 22

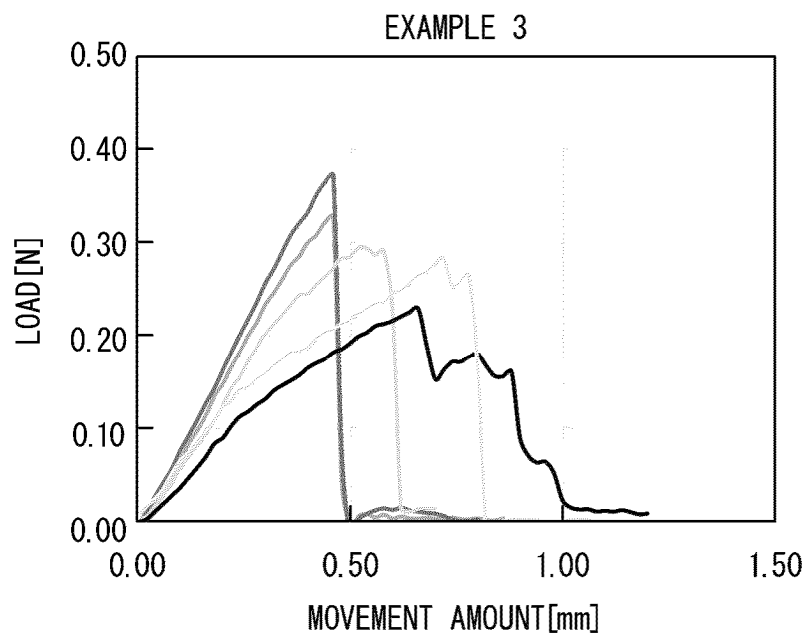


FIG. 23

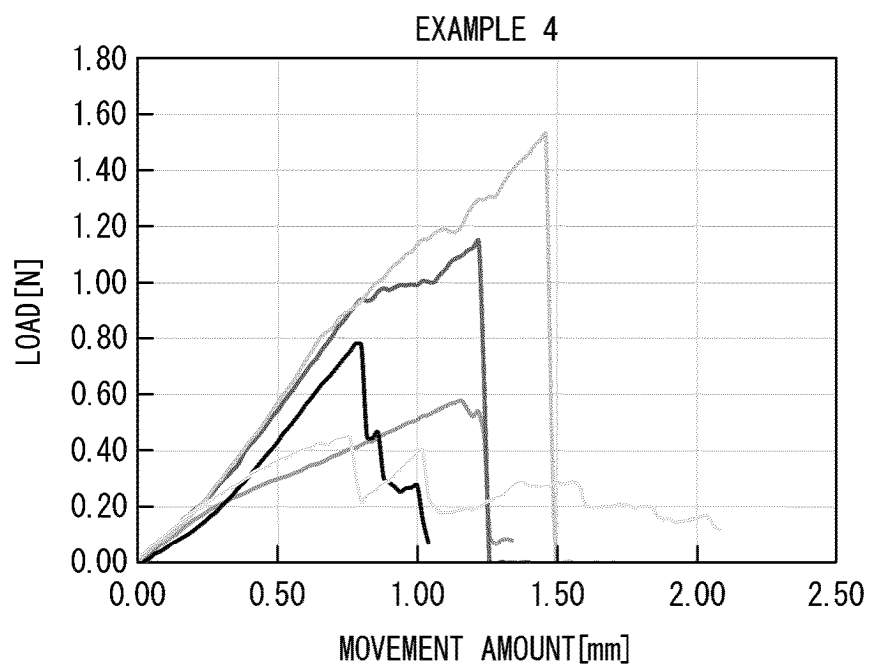


FIG. 24

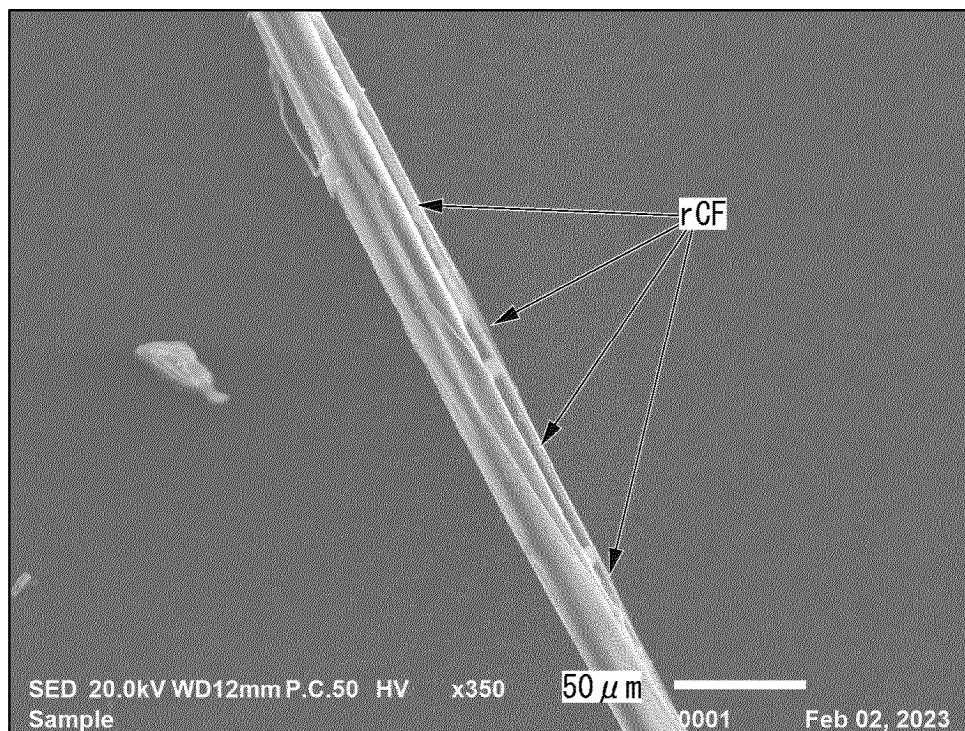


FIG. 25

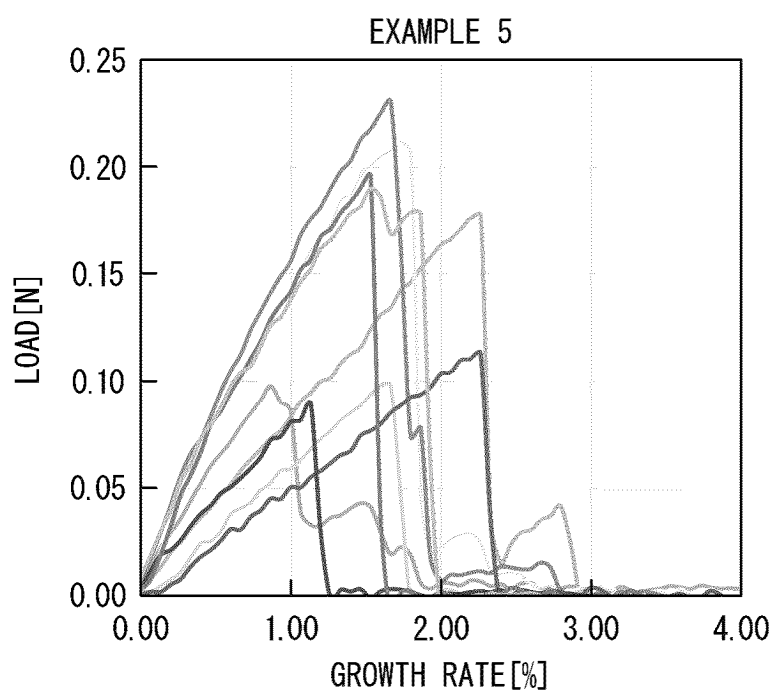


FIG. 26

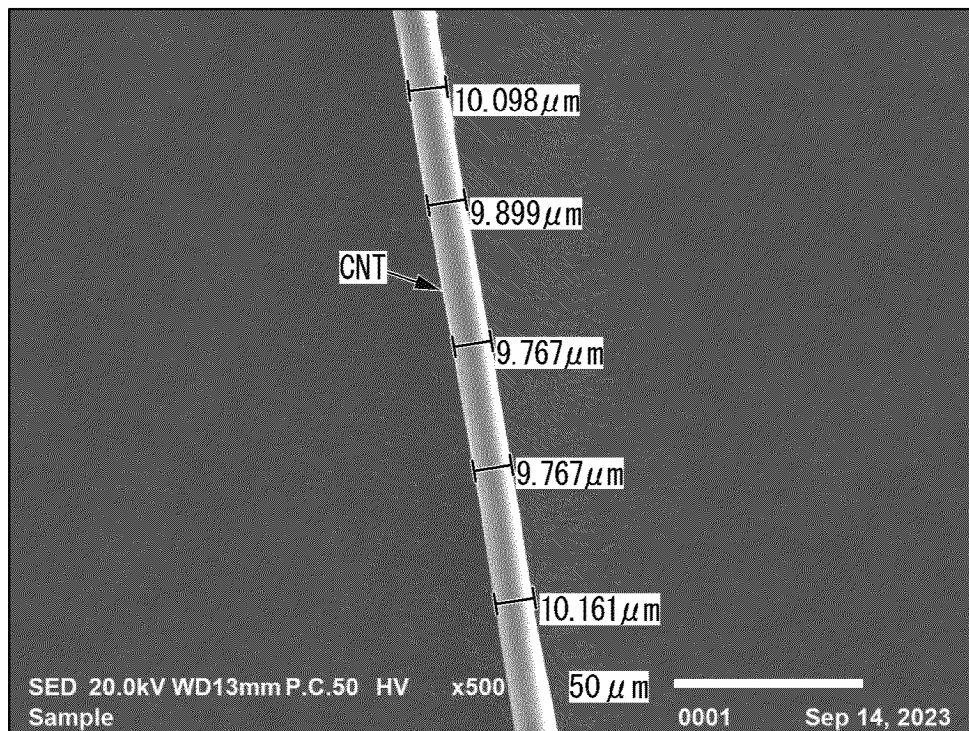


FIG. 27

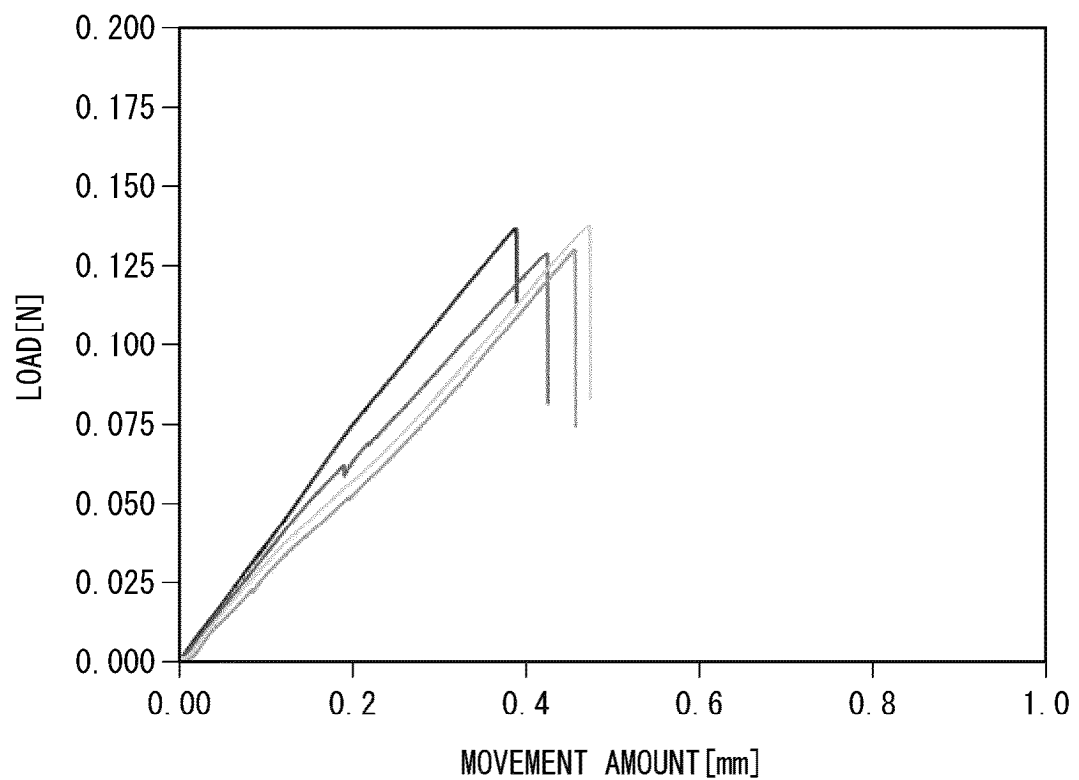
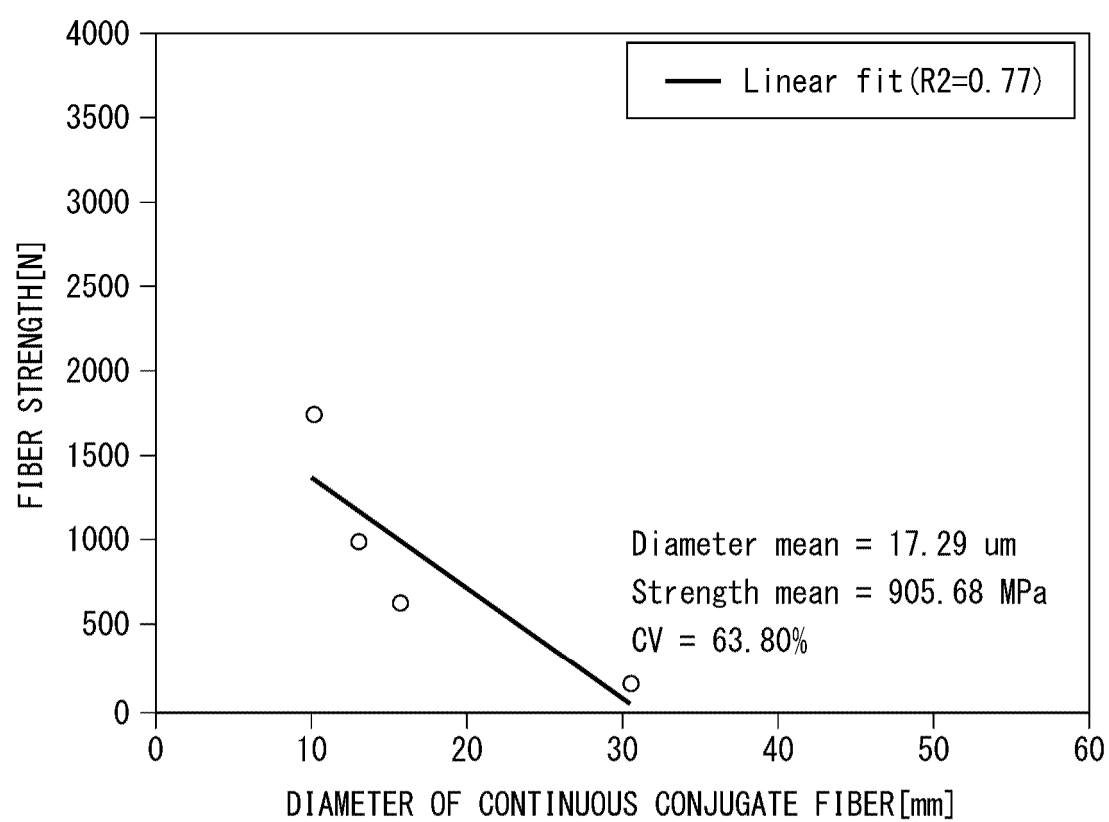


FIG. 28



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/009603

A. CLASSIFICATION OF SUBJECT MATTER

D02G 3/36(2006.01)i; **D01F 9/12**(2006.01)i; **D02G 3/16**(2006.01)i
 FI: D02G3/36; D01F9/12; D02G3/16

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)

D01F1/00-13/04; D02G1/00-3/48; D06M10/00-23/18

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

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.
X	WO 2019/240094 A1 (NITTA CORPORATION) 19 December 2019 (2019-12-19) claims 1, 5, example 1, paragraphs [0014], [0017], [0111], [0113]	1-5
X	JP 2013-76198 A (NITTA CORPORATION) 25 April 2013 (2013-04-25) claims 1, 6, paragraphs [0019], [0030], [0035]	1-5
X	US 2016/0024262 A1 (THE BOARD OF REGENTS) 28 January 2016 (2016-01-28) claims 1, 5, paragraphs [0017], [0036], [0083]	1-6
X	WO 2017/131061 A1 (HITACHI ZOSEN CORP.) 03 August 2017 (2017-08-03) claims 1, 2, 8, paragraphs [0002], [0026], [0049], [0170]	1-12, 17
A	entire text	13-16
X	JP 2014-169521 A (HONDA MOTOR CO., LTD.) 18 September 2014 (2014-09-18) claims 1, 5, paragraphs [0007], [0030]	1-12, 17
A	entire text	13-16

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

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“&” document member of the same patent family

Date of the actual completion of the international search

16 May 2024

Date of mailing of the international search report

28 May 2024

Name and mailing address of the ISA/JP

Japan Patent Office (ISA/JP)
 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915
 Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2024/009603

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2020/241615 A1 (LINTEC CORPORATION) 03 December 2020 (2020-12-03) claims 1, 2, 7, 10	1-12, 17
A	entire text	13-16
A	WO 2017/033683 A1 (KYUSHU UNIVERSITY) 02 March 2017 (2017-03-02) paragraph [0003]	2, 11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/009603

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2019/240094 A1	19 December 2019	US 2021/0230386 A1 claims 1, 5, example 1, paragraphs [0014], [0046], [0146], [0148]	
JP 2013-76198 A	25 April 2013	(Family: none)	
US 2016/0024262 A1	28 January 2016	(Family: none)	
WO 2017/131061 A1	03 August 2017	US 2021/0002794 A1 claims 1, 2, 8, paragraphs [0002], [0028], [0057], [0179]	
JP 2014-169521 A	18 September 2014	US 2014/0217643 A1 claims 1, 5, paragraphs [0008], [0040]	
WO 2020/241615 A1	03 December 2020	US 2022/0220641 A1 claims 1, 2, 7, 10	
WO 2017/033683 A1	02 March 2017	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2023042047 A [0002]
- JP 2010163536 A [0008]
- JP H699160 A [0008]