



(11) **EP 3 348 684 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
18.07.2018 Bulletin 2018/29

(51) Int Cl.:
D01F 9/22 (2006.01) D06M 101/40 (2006.01)

(21) Application number: **17000054.1**

(22) Date of filing: **12.01.2017**

(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 MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(72) Inventor: **Wang, Chih-Yung**
Taoyuan City (TW)

(74) Representative: **Zeitler Volpert Kandlbinder**
Patent- und Rechtsanwälte Partnerschaft mbB
Herrnstrasse 44
80539 München (DE)

(71) Applicant: **UHT Unitech Co., Ltd**
Taoyuan City (TW)

Remarks:

Amended claims in accordance with Rule 137(2) EPC.

(54) **CARBON FIBER MANUFACTURING METHOD AND CARBON FIBER MANUFACTURING APPARATUS**

(57) A carbon fiber manufacturing method and a carbon fiber manufacturing apparatus are provided. A carbon fiber precursor fiber bundle (70A) is performed with a high-temperature carbonization step to form a carbon fiber (70B), and then the carbon fiber (70B) is performed with a plasma surface treatment so that the surface of the carbon fiber (70B) is formed with a plasma-modified configuration (71) which is relatively rougher. Finally, the surface of the carbon fiber (70B) is coated with a resin oiling agent (80) to obtain the carbon fiber (70B) having the resin oiling agent (80) thereon. Particularly, through a plasma surface treatment step, the surface of the carbon fiber (70B) is roughened and provided with functional groups, which is beneficial to enhance the interface bonding of the resin oiling agent (80) and the carbon fiber (70B). The structure of the carbon fiber (70B) is more stable and reliable. The cost of the carbon fiber production equipment and the working time can be reduced effectively.

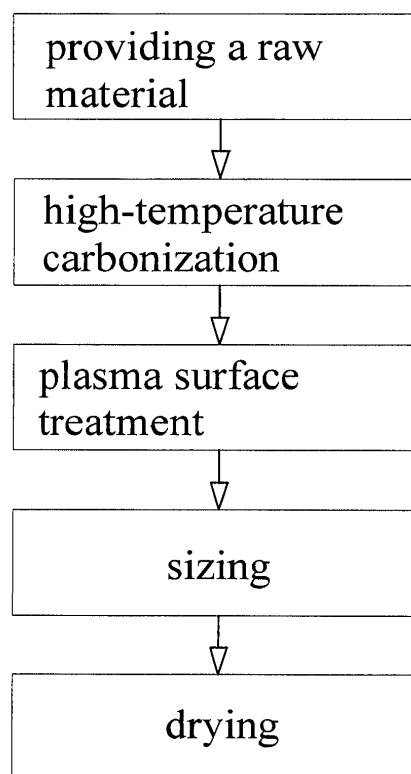


FIG.1

Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a carbon fiber manufacturing technique, and more particularly to a carbon fiber manufacturing method and a carbon fiber manufacturing apparatus which can greatly improve the sizing quality of a carbon fiber and effectively reduce the cost of the carbon fiber production equipment and the working time.

BACKGROUND OF THE INVENTION

10 [0002] Carbon fibers are classified into carbon fibers or graphite fibers according to their carbon contents, which have excellent mechanical properties and electrical properties and can be widely used in various applications. A conventional carbon fiber is achieved by bundling precursor fibers, such as polyacrylonitrile fibers, to form a carbon fiber precursor fiber bundle, and then the carbon fiber precursor fiber bundle is calcined (high-temperature carbonization) to form the carbon fiber.

15 [0003] There are various precursor fibers of carbon fibers on the market, such as rayon, poly vinyl alcohol, vinylidene chloride, polyacrylonitrile (PAN), pitch, and the like. In general, polyacrylonitrile (PAN) is used as the raw material of carbon fibers. The manufacturing steps are generally as follows: PAN raw material (precursor fiber) → pre-oxidation → high-temperature carbonization → surface treatment → sizing.

20 [0004] In the carbonization step, the carbon fiber precursor fiber bundles are heated to form carbon fibers or graphite fibers by different heating apparatuses according to the application of the carbon fibers. In principle, the carbon content of the fibers of graphite fibers is 90% or more, forming a two-dimensional carbocyclic planar net structure and a graphite layer structure having parallel layers. The results show that the crystalline region of a high-strength carbon fiber is composed of 5-6 graphite layers, and the crystalline region of a high-strength and high-modulus carbon fiber is composed

25 of 10-20 graphite layers. Theoretically and practically, it is pointed out that the larger the crystalline thickness of the graphite layer is, the higher the tensile modulus of the carbon fiber is.

[0005] On the other hand, the surface of the carbon fiber after the high-temperature carbonization step is usually coated with a layer of oiling agent (a resin oiling agent is generally used, it is called as a sizing step) before it leaves the factory. The layer of oiling agent is used to protect the fiber from breakage due to friction in the subsequent step to affect

30 the overall quality of the carbon fiber. The surfaces of untreated carbon fibers adsorb impurities thereon. Since these impurities are present between the surface of the carbon fiber and the resin oiling agent, the adhesion between the carbon fiber and the resin oiling agent is insufficient, and the purpose of protecting the fiber cannot be achieved

[0006] Furthermore, in the high-temperature carbonization step, the surface of the carbon fiber is excessively finely formed due to high-temperature sintering, and there are few functional groups on the surface. As a result, the fiber and

35 the resin oiling agent cannot be bonded fully in the sizing step. It is known that a heat treatment or electrolysis technique can be applied to the surface treatment of the fiber after the high-temperature carbonization step, and then the sizing step is performed in order to improve the bonding of the fiber and the resin oiling agent.

[0007] However, when the surface treatment of the carbon fiber is performed by means of heat treatment, the carbon fiber is treated at a temperature in the range of 500°C to 800°C for 1-10 minutes. A relatively long period of time is required. Besides, the heat treatment is always performed with a large number of fibers at a time, so it is difficult to control the processing quality. When the surface treatment of the carbon fiber is performed by means of electrolysis, at least one drying process is required before the surface of the fiber is coated with the oiling agent. This also takes more time. Moreover, a change of the electrolyte may affect the processing quality. Even the surface of the fiber may have depositions.

40 [0008] Accordingly, the inventor of the present invention has devoted himself based on his many years of practical experiences to solve these problems.

SUMMARY OF THE INVENTION

50 [0009] In view of the problems of the prior art, the primary object of the present invention is to provide a carbon fiber manufacturing method which can greatly improve the sizing quality of a carbon fiber and effectively reduce the cost of the carbon fiber production equipment and the working time.

[0010] In order to achieve the forgoing object, the carbon fiber manufacturing method of the present invention comprises providing a raw material step, providing a carbon fiber precursor fiber bundle; performing a high-temperature carbonization step, the carbon fiber precursor fiber bundle being heated to form a carbon fiber having a predetermined carbon content; performing a plasma surface treatment step, a plasma gas flow with a predetermined power being provided to act on the carbon fiber at a predetermined time so that a surface of the carbon fiber is formed with a plasma-modified configuration; performing a sizing step, the plasma-modified configuration being coated with a resin oiling agent; and performing

a drying step, the resin oiling agent coated on the plasma-modified configuration being processed with drying so that the resin oiling agent is firmly adhered to the surface of the carbon fiber.

[0011] In the carbon fiber manufacturing method of the present invention, through the plasma surface treatment step, the surface of the carbon fiber is roughened and provided with functional groups, which is beneficial to enhance the interface bonding of the resin oiling agent and the carbon fiber in the subsequent sizing step so as to improve the sizing quality of the carbon fiber greatly. The structure of the carbon fiber is more stable and reliable. The plasma surface treatment belongs to a dry-type and fast surface treatment technique to effectively reduce the cost of the carbon fiber production equipment and the working time.

[0012] Preferably, in the high-temperature carbonization step, the carbon fiber precursor fiber bundle is guided into a chamber. The chamber is formed with at least one microwave field concentration area therein, and is provided with a gas supply assembly to supply an inert gas and a microwave generating assembly to supply a high-frequency microwave. Under the protection of the inert gas atmosphere, the electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle passing through the microwave field concentration area.

[0013] Preferably, the chamber is provided with at least one pair of microwave-sensitive materials.

[0014] Preferably, the microwave-sensitive materials are one of graphite, carbide, magnetic compound, nitride, and ionic compound or a combination thereof.

[0015] Preferably, the inert gas is nitrogen, argon, helium, or a combination thereof.

[0016] Preferably, the frequency of the high-frequency microwave is in the range of 300-30,000 MHz, and its microwave power density is in the range of 1-1000kW/m³.

[0017] Preferably, the chamber is an elliptic chamber.

[0018] Alternatively, the chamber is a flat panel chamber.

[0019] Preferably, in the plasma surface treatment step, the plasma gas flow with a power of 100-10000 watts acts on the carbon fiber for 10-1000 milliseconds.

[0020] Alternatively, in the plasma surface treatment step, an atmospheric plasma gas flow with a power of 100-10000 watts acts on the carbon fiber for 10-1000 milliseconds.

[0021] Alternatively, in the plasma surface treatment step, a low-pressure plasma gas flow with a power of 100-10000 watts acts on the carbon fiber for 10-1000 milliseconds.

[0022] Alternatively, in the plasma surface treatment step, a microwave plasma gas flow with a power of 100-10000 watts acts on the carbon fiber for 10-1000 milliseconds.

[0023] Alternatively, in the plasma surface treatment step, a glow plasma gas flow with a power of 100-10000 watts acts on the carbon fiber for 10-1000 milliseconds.

[0024] Preferably, the carbon fiber precursor fiber bundle has a surface not processed with a pre-oxidation treatment.

[0025] Alternatively, the carbon fiber precursor fiber bundle has a surface processed with a pre-oxidation treatment in advance.

[0026] Preferably, the resin oiling agent is a thermosetting resin oiling agent.

[0027] Alternatively, the resin oiling agent is a thermoplastic resin oiling agent.

[0028] Preferably, the carbon content of the carbon fiber is in the range of 80%-90%.

[0029] In order to achieve the forgoing object, the carbon fiber manufacturing apparatus of the present invention comprises a feeding module, a receiving module, a high-temperature carbonization module, a plasma surface treatment module, and a sizing module. The receiving module is disposed in the vicinity of the feeding module. The feeding module and the receiving module constitute a carbon fiber drag route. The high-temperature carbonization module is disposed at the carbon fiber drag route and located between the feeding module and the receiving module for heating the carbon fiber drag route. The plasma surface treatment module is disposed at the carbon fiber drag route and located between the high-temperature carbonization module and the receiving module for supplying a plasma gas flow to the carbon fiber drag route. The sizing module is disposed at the carbon fiber drag route and located between the plasma surface treatment module and the receiving module for coating a resin oiling agent on the surface of a carbon fiber.

[0030] Thereby, the carbon fiber manufacturing apparatus of the present invention can be operated in the integrated operation of the feeding module, the high-temperature carbonization module, the plasma surface treatment module, the sizing module, and the receiving module. A carbon fiber precursor fiber bundle released from the feeding module is sequentially processed at a predetermined speed to perform the steps of high-temperature carbonization, plasma surface treatment, sizing, and so on, in a relatively more active and reliable manner. The carbon fiber precursor fiber bundle is heated to form the carbon fiber, and then the surface of the carbon fiber is formed with the resin oiling agent. Particularly, through the plasma surface treatment module, the surface of the carbon fiber is roughened and provided with functional groups, which is beneficial to enhance the interface bonding of the resin oiling agent and the carbon fiber in the subsequent sizing procedure so as to improve the sizing quality of the carbon fiber greatly. The structure of the carbon fiber is more stable and reliable. The plasma surface treatment belongs to a dry-type and fast surface treatment technique to effectively reduce the cost of the carbon fiber production equipment and the working time.

[0031] Preferably, the high-temperature carbonization module has a chamber for the carbon fiber drag route or the carbon fiber precursor fiber bundle to pass therethrough. The chamber is formed with at least one microwave field concentration area and supplies an inert gas and a high-frequency microwave. Under the protection of the inert gas atmosphere, the electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle passing through the microwave field concentration area.

[0032] Preferably, the high-temperature carbonization module has a chamber for the carbon fiber drag route or the carbon fiber precursor fiber bundle to pass therethrough. The chamber is formed with at least one microwave field concentration area and provided with a gas supply assembly to supply an inert gas and a microwave generating assembly to supply a high-frequency microwave. Under the protection of the inert gas atmosphere, the electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle passing through the microwave field concentration area. The plasma surface treatment module is provided with at least one plasma generator.

[0033] Preferably, the plasma surface treatment module is provided with at least one plasma generator located at upper and lower positions of the carbon fiber drag route, respectively.

[0034] Preferably, the chamber is an elliptic chamber.

[0035] Preferably, the chamber is an elliptic chamber, and the chamber is provided with at least one pair of microwave-sensitive materials.

[0036] Alternatively, the chamber is a flat plate chamber.

[0037] Alternatively, the chamber is a flat plate chamber, and the chamber is provided with at least one pair of microwave-sensitive materials.

[0038] Preferably, the plasma generator is able to generate the plasma gas flow having a power in the range of 100-10000 Watts.

[0039] Alternatively, the plasma generator is able to generate an atmospheric plasma gas flow having a power in a range of 100-10000 Watts.

[0040] Alternatively, the plasma generator is able to generate a low-pressure plasma gas flow having a power in the range of 100-10000 Watts.

[0041] Alternatively, the plasma generator is able to generate a microwave plasma gas flow having a power in the range of 100-10000 Watts.

[0042] Alternatively, the plasma generator is able to generate a glow plasma gas flow having a power in the range of 100-10000 Watts.

[0043] Preferably, the sizing module is provided with at least one reservoir.

[0044] Preferably, the carbon fiber manufacturing apparatus further comprises a drying module. The drying module is disposed at the carbon fiber drag route between the sizing module and the receiving module for the resin oiling agent to be adhered to the surface of the carbon fiber firmly.

[0045] Specifically, through plasma surface treatment, the surface of the carbon fiber can be roughened and provided with the functional groups, which is beneficial to enhance the interface bonding of the resin oiling agent and the carbon fiber in the subsequent sizing step. The structure of the carbon fiber is more stable and reliable. By the microwave focusing heating way, the same apparatus can be applied to a carbon fiber precursor fiber bundle whose surface has not been processed with a pre-oxidation treatment or a carbon fiber precursor fiber bundle whose surface has been processed with a pre-oxidation treatment in advance. By simply adjusting the microwave power, the apparatus can be used to produce general carbon fibers or high modulus carbon fibers (graphite fibers) so as to reduce the cost of the carbon fiber production equipment and the working time effectively.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046]

FIG. 1 is a flow diagram of a carbon fiber manufacturing method of the present invention;

FIG. 2 is a structural schematic view of a high-temperature carbonization module in accordance with an embodiment of the present invention;

FIG. 3 is a sectional schematic view of a carbon fiber after finishing a plasma surface treatment step of the present invention;

FIG. 4 is a sectional schematic view of a carbon fiber after finishing a sizing step of the present invention;

FIG. 5 is a structural schematic view of a high-temperature carbonization module in accordance with another embodiment of the present invention;

FIG. 6a illustrates a SEM image of an object to be tested without plasma treatment; and

FIG. 6b illustrates a SEM image of an object to be tested with the plasma treatment.

FIG. 7 is a structural schematic view of a carbon fiber manufacturing apparatus in accordance with a first embodiment of the present invention; and

FIG. 8 is a structural schematic view of a carbon fiber manufacturing apparatus in accordance with a second embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0047] Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings.

[0048] The present invention discloses a carbon fiber manufacturing method which can greatly improve the sizing quality of carbon fibers and effectively reduce the cost of the carbon fiber production equipment and the working time. As shown in FIG. 1, the carbon fiber manufacturing method of the present invention comprises providing a raw material step, performing a high-temperature carbonization step, performing a plasma surface treatment step, and performing a sizing step. The carbon fiber manufacturing method further comprises performing a drying step after the sizing step. Referring to FIG. 1 through FIG. 5, the steps are described in details as below.

[0049] In the step of providing the raw material, a carbon fiber precursor fiber bundle is provided to be processed to form a carbon fiber. In practice, the carbon fiber precursor fiber bundle may be formed of rayon, poly vinyl alcohol, vinylidene chloride, polyacrylonitrile (PAN), pitch, and the like. The surface of the carbon fiber precursor fiber bundle may have not been processed with a pre-oxidation treatment or have been processed with a pre-oxidation treatment in advance.

[0050] In the high-temperature carbonization step, the carbon fiber precursor fiber bundle is heated to form the carbon fiber having a predetermined carbon content. In practice, as shown in FIG. 2, the carbon fiber precursor fiber bundle 70A is guided into a chamber 31 of a high-temperature carbonization module 30. The chamber 31 is formed with at least one microwave field concentration area 311 therein, and is provided with a gas supply assembly 32 to supply an inert gas and a microwave generating assembly 33 to supply a high-frequency microwave. Under the protection of the inert gas atmosphere, the electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle 70A passing through the microwave field concentration area 311, enabling the carbon fiber precursor fiber bundle to form the carbon fiber 70B having a predetermined carbon content. The carbon content of the carbon fiber 70B is in the range of 80%-90%.

[0051] In the plasma surface treatment step, a plasma gas flow with a predetermined power is provided to act on the carbon fiber 70B at a predetermined time, such that the surface of the carbon fiber 70B is formed with a plasma-modified configuration 71, shown in FIG. 3, which is rougher or has more functional groups relative to the carbon fiber precursor fiber bundle 70A.

[0052] In the sizing step, the plasma-modified configuration 71 on the surface of the carbon fiber 70B is coated with a resin oiling agent 80, so that the surface of the carbon fiber 70B has the resin oiling agent 80, as shown in FIG. 4. In practice, the resin oiling agent 80 is coated on the surface of the carbon fiber 70B by soaking or immersing. The resin oiling agent 80 may be a thermosetting resin oiling agent or a thermoplastic resin oiling agent.

[0053] In the drying step, a drying treatment is applied to the resin oiling agent 80 coated on the plasma-modified configuration 71 so that the resin oiling agent 80 is firmly adhered to the surface of the carbon fiber 70B. In practice, the drying treatment is carried out by ultraviolet irradiation, cooling, drying or air-drying for the resin oiling agent to be bonded to the surface of the carbon fiber.

[0054] In the plasma surface treatment step, an atmospheric plasma gas flow, a low-pressure plasma gas flow, a microwave plasma gas flow, or a glow plasma gas flow with a power of 100-10000 watts may be used to act on the carbon fiber 10B for 10-1000 milliseconds. Since the plasma gas flow contains particles having energy, the impurities that originally adhere to the surface of the carbon fiber 10B can be broken to form small molecules by the impact of the plasma gas flow through the physical reaction (collision) of the plasma gas flow, and then the small molecules are blown away from the surface of the carbon fiber 70B by the air flow, so that the surface of the carbon fiber 70B is clean. In the sizing step, the resin oiling agent 80 can be completely in contact with the carbon fiber 70B to increase the bonding effect. In addition, the impact of the plasma gas flow will also form the plasma-modified configuration 71 on the surface of the carbon fiber 70B. The plasma-modified configuration 71 is rougher relative to the carbon fiber precursor fiber

bundle 70A, and is further formed with pores. The surface of the carbon fiber 70B is roughened or formed with the pores, which is beneficial to increase the contact area between the resin oiling agent 80 and the carbon fiber 70B in the subsequent sizing step. The resin oiling agent 80 penetrates into the pores, and the resin oiling agent 80 is anchored between the pores to form an anchor effect to enhance the bonding effect of the resin oiling agent 80 and the carbon fiber 70B.

[0055] The plasma gas flow also makes the surface of the carbon fiber 70B generate a chemical reaction at the same time, so that at least one functional group (such as -OH, -N, etc.) is added to the surface of the carbon fiber 70B. In the sizing step, the surface tension of the surface of the carbon fiber 70B is increased due to the presence of the functional group, which is beneficial to improve the wetting effect for the resin oiling agent 80 to be coated on the carbon fiber 70B. That is, the contact angle of the resin oiling agent 80 to the carbon fiber 70B becomes small, so that the resin oiling agent 80 can be quickly or instantaneously coated on the carbon fiber 70B, and the speed of the sizing step is increased, thereby accelerating the overall production speed of the carbon fiber 70B. The presence of the functional group such as the OH group reacts with the resin oiling agent 80, such as epoxy resin (Epoxy), to generate hydrogen bonding, thereby increasing the bonding effect.

[0056] Thereby, in the carbon fiber manufacturing method of the present invention, through the plasma surface treatment step, the surface of the carbon fiber 70B is roughened and provided with functional groups, which is beneficial to enhance the interface bonding of the resin oiling agent 80 and the carbon fiber 70B in the subsequent sizing step so as to improve the sizing quality of the carbon fiber 70B greatly. The structure of the carbon fiber is more stable and reliable. The plasma surface treatment belongs to a dry-type and fast surface treatment technique to effectively reduce the cost of the carbon fiber production equipment and the working time.

[0057] Furthermore, the foregoing inert gas may be nitrogen, argon, helium, or a combination thereof. The frequency of the high-frequency microwave may be in the range of 300-30,000 MHz, and its microwave power density may be in the range of 1-1000kW/m³.

[0058] In the embodiment as shown in FIG. 2, the chamber 31 of the high-temperature carbonization module 30 may be an elliptic chamber, or the chamber 31 may be a flat plate chamber as shown in FIG. 5. As shown in FIG. 5, whatever the chamber 31 is, the chamber 31 is provided with a pair of microwave-sensitive materials 34 therein, thereby enhancing the focusing effect on the microwave field in order to further accelerate the high-temperature carbonization process. In practice, the microwave-sensitive materials 34 may be one of graphite, carbide, magnetic compound, nitride, and ionic compound or a combination thereof.

[0059] Due to the resonant effect of microwave heating, the carbonization of the carbon fiber is enhanced rapidly and more crystalline carbons are formed and stacked, which leads to the formation of larger graphite crystalline molecules, namely, larger graphite crystalline thickness, while deriving a higher microwave induction heating effect is derived. Such a cycle generates an autocatalytic reaction, enabling the carbon fiber to be rapidly heated to the graphitization temperature (1500- 3000°C), and carbon atoms are reconstructed and rearranged more rapidly to form a graphite layer.

[0060] In other words, the same apparatus can be applied to a carbon fiber precursor fiber bundle whose surface has not been processed with a pre-oxidation treatment or a carbon fiber precursor fiber bundle whose surface has been processed with a pre-oxidation treatment in advance. It is only necessary to adjust the microwave power for the production, the apparatus can be used to produce general carbon fibers (1000-1500°C) or high modulus carbon fibers (graphite fibers).

[0061] In a preferred embodiment, an object to be tested that the resin oiling agent after the drying step is firmly adhered to the surface of the carbon fiber, and the treatment conditions in the plasma surface treatment step are shown in Table 1 below:

Table 1: the conditions of the plasma surface treatment

plasma gas consumption	N ₂	200	L/min
	CDA	0.4	L/min
plasma gas amount	200.4		L/min
plasma power	0~1000		W
plasma surface treatment time	0.025~0.100		sec.
carbon fiber yarn width	7		mm
yarn per unit time receiving capacity	0.28		J/s
distance	1		mm

[0062] The ILSS strength (interlayer bonding force) was measured for an object to be tested in an environment of a temperature of 23°C and a humidity of 50% RH by using an INSTRON measuring machine according to ASTM 2344,

and the results are shown in Table 2 below:

Table 2: the relationship between the plasma surface treatment power (W), the processing time (sec.), and the interlayer bonding force (MPa) (epoxy resin used as the resin oiling agent) of PAN carbon fiber 12K.

plasma power (W) of surface treatment	interlayer bonding force (ILSS)(MPa)		
	0.025 sec.	0.075 sec.	0.100 sec.
0(untreated)	70	70	70
250	71	73	75
500	73	76	81
750	75	81	85
900	79	86	88
1000	83	89	91

[0063] As can be seen from Table 2, the carbon fiber without the plasma surface treatment, the interlayer bonding force of the object to be tested is only 70MPa. With an increase of the plasma power, for example, the processing time is 0.075 seconds and the plasma power is increased from the untreated (0W, without plasma power) to 1000W, the interlayer bonding force is increased from 70MPa to 89MPa. That is, the interlayer bonding force is increased to 127%.

[0064] In the sizing step, the epoxy resin is used as the resin oiling agent, and the carbon fiber is used as the carbon fiber 70B. FIG. 6a shows a SEM image of the object to be tested without the plasma treatment. FIG. 6b shows a SEM image of the object to be tested with the plasma treatment. As shown in FIG. 6a, the SEM image of the object to be tested without the plasma surface treatment illustrates a void H between the resin oiling agent 80 and the carbon fiber 70B because the surface of the carbon fiber 70B is smooth and doesn't have functional groups. The void H causes a decrease in the strength of the object to be tested. That is to say, the bonding force between the carbon fiber and the resin oiling agent is insufficient for protecting the fiber.

[0065] As shown in FIG. 6b, the SEM image of the object to be tested with the plasma surface treatment illustrates that there is no void between the resin oiling agent 80 and the carbon fiber 70B because the surface of the carbon fiber 70B is rough and has functional groups (such as -OH, -N, etc.). The resin oiling agent 80 and the carbon fiber 70B are bonded tightly, so that the strength of the object to be tested is enhanced. That is, the adhesion between the carbon fiber and the resin oiling agent is enhanced, so that the purpose of protecting the fiber can be achieved.

[0066] In order to implement the aforesaid carbon fiber manufacturing method, the present invention further discloses a carbon fiber manufacturing apparatus which can greatly improve the sizing quality of carbon fibers and effectively reduce the cost of the carbon fiber production equipment and the working time. As shown in FIG. 7, the carbon fiber manufacturing apparatus of the present invention comprises a feeding module 10, a receiving module 20, a high-temperature carbonization module 30, a plasma surface treatment module 40, and a sizing module 50.

[0067] The feeding module 10 is to perform the step of providing a raw material in the carbon fiber manufacturing method, and is used to supply a carbon fiber precursor fiber bundle 70A to be processed into a carbon fiber 70B.

[0068] The receiving module 20 is disposed in the vicinity of the feeding module 10, and corresponds to the feeding module 10 to constitute a carbon fiber drag route. The receiving module 20 includes a yarn winding assembly 21 to receive the carbon fiber 70B. The yarn winding assembly 21 performs a drag action on the carbon fiber 70B to be received.

[0069] The high-temperature carbonization module 30 is to perform the high-temperature carbonization step in the carbon fiber manufacturing method. The high-temperature carbonization module 30 is disposed at the carbon fiber drag route between the feeding module 10 and the receiving module 20 for heating the carbon fiber precursor fiber bundle 70A, enabling the carbon fiber precursor fiber bundle 70A to become the carbon fiber 70B having a predetermined carbon content.

[0070] The plasma surface treatment module 40 is to perform the plasma surface treatment step in the carbon fiber manufacturing method. The plasma surface treatment module 40 is disposed at the carbon fiber drag route between the high-temperature carbonization module 30 and the receiving module 20 to provide a plasma gas flow with a predetermined power to act on the carbon fiber 70B, such that the surface of the carbon fiber 70B is formed with a plasma-modified configuration 71 which is rougher or has more functional groups relative to the carbon fiber precursor fiber bundle 70A.

[0071] The sizing module 50 is to perform the sizing step in the carbon fiber manufacturing method. The sizing module 50 is disposed at the carbon fiber drag route between the plasma surface treatment module 40 and the receiving module 20 for the plasma-modified configuration 71 on the surface of the carbon fiber 70B to be coated with a resin oiling agent 80. The sizing module 50 is provided with at least one reservoir 51 for storing the resin oiling agent 80.

[0072] As shown in FIG. 8, the carbon fiber manufacturing apparatus of the present invention may further comprise a drying module 60. The drying module 60 is to perform the drying step in the carbon fiber manufacturing method. The drying module 60 is disposed at the carbon fiber drag route between the sizing module 50 and the receiving module 20 for the resin oiling agent 80 to be firmly adhered to the surface of the carbon fiber 70B. In practice, the drying module 60 is provided with at least one blast furnace 61 to generate hot blast.

[0073] Thereby, the carbon fiber manufacturing apparatus of the present invention can be operated in the integrated operation of the feeding module 10, the high-temperature carbonization module 30, the plasma surface treatment module 40, the sizing module 50, and the receiving module 20. The carbon fiber precursor fiber bundle 70A released from the feeding module 10 is sequentially processed at a predetermined speed to perform the steps of high-temperature carbonization, plasma surface treatment, sizing, and so on, in a relatively more active and reliable manner. The carbon fiber precursor fiber bundle 70A is heated to form the carbon fiber 70B, and then the surface of the carbon fiber 70B is formed with the resin oiling agent 80.

[0074] The plasma surface treatment module 40 is provided with at least one plasma generator 41 for generating a plasma gas flow. In an embodiment, the plasma surface treatment module 40 is provided with at least one plasma generator 41 disposed at the upper and lower positions of the carbon fiber drag route respectively for generating a plasma gas flow to act on the surface of the carbon fiber 70B.

[0075] Compared to the prior art, through the carbon fiber manufacturing method and the carbon fiber manufacturing apparatus of the present invention, the surface of the carbon fiber can be roughened and provided with the functional groups by the plasma surface treatment step, which is beneficial to enhance the interface bonding of the resin oiling agent and the carbon fiber in the subsequent sizing step. The structure of the carbon fiber is more stable and reliable to improve the quality of the carbon fiber, thereby accelerating the overall production speed of the carbon fiber. By the microwave focusing heating way, the same apparatus can be applied to a carbon fiber precursor fiber bundle whose surface has not been processed with a pre-oxidation treatment or a carbon fiber precursor fiber bundle whose surface has been processed with a pre-oxidation treatment in advance. By simply adjusting the microwave power, the apparatus can be used to produce general carbon fibers or high modulus carbon fibers (graphite fibers) so as to reduce the cost of the carbon fiber production equipment and the working time effectively.

[0076] Although particular embodiments of the present invention have been described in detail for purposes of illustration, various modifications and enhancements may be made without departing from the spirit and scope of the present invention. Accordingly, the present invention is not to be limited except as by the appended claims.

Claims

1. A carbon fiber manufacturing method, comprising:

providing a raw material step, providing a carbon fiber precursor fiber bundle (70A);
 performing a high-temperature carbonization step, the carbon fiber precursor fiber bundle (70A) being heated to form a carbon fiber (70B) having a predetermined carbon content;
 performing a plasma surface treatment step, a plasma gas flow with a predetermined power being provided to act on the carbon fiber (70B) at a predetermined time so that a surface of the carbon fiber (70B) is formed with a plasma-modified configuration (71);
 performing a sizing step, the plasma-modified configuration (71) being coated with a resin oiling agent (80); and
 performing a drying step, the resin oiling agent (80) coated on the plasma-modified configuration (71) being processed with drying so that the resin oiling agent (80) is firmly adhered to the surface of the carbon fiber (70B).

2. The carbon fiber manufacturing method as claimed in claim 1, wherein in the high-temperature carbonization step, the carbon fiber precursor fiber bundle (70A) is guided into a chamber (31), the chamber (31) is formed with at least one microwave field concentration area (311) therein and is provided with a gas supply assembly (32) to supply an inert gas and a microwave generating assembly (33) to supply a high-frequency microwave, under the protection of the inert gas atmosphere, an electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle (70A) passing through the microwave field concentration area (311).

3. The carbon fiber manufacturing method as claimed in claim 2, wherein the chamber (31) is provided with at least one pair of microwave-sensitive materials (34).

4. The carbon fiber manufacturing method as claimed in claim 3, wherein the microwave-sensitive materials (34) are one of graphite, carbide, magnetic compound, nitride, and ionic compound or a combination thereof.

5. The carbon fiber manufacturing method as claimed in claim 2, wherein the inert gas is nitrogen, argon, helium, or a combination thereof.
6. The carbon fiber manufacturing method as claimed in claim 2, wherein the frequency of the high-frequency microwave is in the range of 300-30,000 MHz, and its microwave power density is in the range of 1-1000kW/m³.
7. The carbon fiber manufacturing method as claimed in claim 2, wherein the chamber (31) is an elliptic chamber.
8. The carbon fiber manufacturing method as claimed in claim 2, wherein the chamber (31) is a flat panel chamber.
9. The carbon fiber manufacturing method as claimed in claim 1, wherein in the plasma surface treatment step, the plasma gas flow, an atmospheric plasma gas flow, a low-pressure plasma gas flow, a microwave plasma gas flow, or a glow plasma gas flow with a power of 100-10000 watts acts on the carbon fiber (70B) for 10-1000 milliseconds.
10. The carbon fiber manufacturing method as claimed in claim 1, wherein the carbon fiber precursor fiber bundle (70A) has a surface not processed with a pre-oxidation treatment.
11. The carbon fiber manufacturing method as claimed in claim 1, wherein the carbon fiber precursor fiber bundle (70A) has a surface processed with a pre-oxidation treatment in advance.
12. The carbon fiber manufacturing method as claimed in claim 1, wherein the resin oiling agent (80) is a thermosetting resin oiling agent.
13. The carbon fiber manufacturing method as claimed in claim 1, wherein the resin oiling agent (80) is a thermoplastic resin oiling agent.
14. The carbon fiber manufacturing method as claimed in claim 1, wherein the carbon content of the carbon fiber (70B) is in the range of 80%-90%.
15. A carbon fiber manufacturing apparatus, comprising:
 - a feeding module (10) and a receiving module (20), the receiving module (20) being disposed in the vicinity of the feeding module (10), the feeding module (10) and the receiving module (20) constituting a carbon fiber drag route;
 - a high-temperature carbonization module (30), disposed at the carbon fiber drag route and located between the feeding module (10) and the receiving module (20) for heating the carbon fiber drag route;
 - a plasma surface treatment module (40), disposed at the carbon fiber drag route and located between the high-temperature carbonization module (30) and the receiving module (20) for supplying a plasma gas flow to the carbon fiber drag route; and
 - a sizing module (50), disposed at the carbon fiber drag route and located between the plasma surface treatment module (40) and the receiving module (20).
16. The carbon fiber manufacturing apparatus as claimed in claim 15, wherein the high-temperature carbonization module (30) has a chamber (31), a gas supply assembly (32), and a microwave generating assembly (33), the carbon fiber drag route passes through the chamber (31), the gas supply assembly (32) is used to supply an inert gas, and the microwave generating assembly (33) is used to supply a high-frequency microwave.
17. The carbon fiber manufacturing apparatus as claimed in claim 16, wherein the plasma surface treatment module (40) is provided with at least one plasma generator (41).
18. The carbon fiber manufacturing apparatus as claimed in claim 16, wherein the plasma surface treatment module (40) is provided with at least one plasma generator (41) located at upper and lower positions of the carbon fiber drag route, respectively.
19. The carbon fiber manufacturing apparatus as claimed in claim 16, wherein the chamber (31) is an elliptic chamber.
20. The carbon fiber manufacturing apparatus as claimed in claim 19, wherein the chamber (31) is provided with at least one pair of microwave-sensitive materials (34).

21. The carbon fiber manufacturing apparatus as claimed in claim 16, wherein the chamber (31) is a flat plate chamber.
22. The carbon fiber manufacturing apparatus as claimed in claim 21, wherein the chamber is provided with at least one pair of microwave-sensitive materials (34).
23. The carbon fiber manufacturing apparatus as claimed in claim 17, wherein the plasma generator is able to generate the plasma gas flow, an atmospheric plasma gas flow, a low-pressure plasma gas flow, a microwave plasma gas flow, or a glow plasma gas flow having a power in the range of 100-10000 watts.
24. The carbon fiber manufacturing apparatus as claimed in claim 15, wherein the sizing module (50) is provided with at least one reservoir (51).
25. The carbon fiber manufacturing apparatus as claimed in claim 15, further comprising a drying module (60), the drying module (60) being disposed at the carbon fiber drag route between the sizing module (50) and the receiving module (20).

Amended claims in accordance with Rule 137(2) EPC.

1. A carbon fiber manufacturing method, comprising;
 providing a raw material step, providing a carbon fiber precursor fiber bundle (70A); performing a high-temperature carbonization step, the carbon fiber precursor fiber bundle (70A) being heated to form a carbon fiber (70B) having a predetermined carbon content;
 performing a plasma surface treatment step, a plasma gas flow with a predetermined power being provided to act on the carbon fiber (70B) at a predetermined time so that a surface of the carbon fiber (70B) is formed with a plasma-modified configuration (71);
 performing a sizing step, the plasma-modified configuration (71) being coated with a resin oiling agent (80); and
 performing a drying step, the resin oiling agent (80) coated on the plasma-modified configuration (71) being processed with drying so that the resin oiling agent (80) is firmly adhered to the surface of the carbon fiber (70B);
 wherein in the high-temperature carbonization step, the carbon fiber precursor fiber bundle (70A) is guided into a chamber (31), the chamber (31) is formed with at least one microwave field concentration area (311) therein and is provided with a gas supply assembly (32) to supply an inert gas and a microwave generating assembly (33) to supply a high-frequency microwave, under the protection of the inert gas atmosphere, an electric field of the high-frequency microwave produces a sensing current to heat up and produce a high temperature quickly with the carbon fiber precursor fiber bundle (70A) passing through the microwave field concentration area (311);
 wherein the chamber (31) is provided with at least one pair of microwave-sensitive materials (34).
2. The carbon fiber manufacturing method as claimed in claim 1, wherein the microwave-sensitive materials (34) are one of graphite, carbide, magnetic compound, nitride, and ionic compound or a combination thereof.
3. The carbon fiber manufacturing method as claimed in claim 1, wherein the inert gas is nitrogen, argon, helium, or a combination thereof.
4. The carbon fiber manufacturing method as claimed in claim 1, wherein the frequency of the high-frequency microwave is in the range of 300-30,000 MHz, and its microwave power density is in the range of 1-1000kW/m³.
5. The carbon fiber manufacturing method as claimed in claim 1, wherein the chamber (31) is an elliptic chamber.
6. The carbon fiber manufacturing method as claimed in claim 1, wherein the chamber (31) is a flat panel chamber.
7. The carbon fiber manufacturing method as claimed in any one of the foregoing claims, wherein in the plasma surface treatment step, the plasma gas flow, an atmospheric plasma gas flow, a low-pressure plasma gas flow, a microwave plasma gas flow, or a glow plasma gas flow with a power of 100-10000 watts acts on the carbon fiber (70B) for 10-1000 milliseconds.
8. The carbon fiber manufacturing method as claimed in any one of the foregoing claims, wherein the carbon fiber precursor fiber bundle (70A) has a surface not processed with a pre-oxidation treatment.

9. The carbon fiber manufacturing method as claimed in any one of claims 1 to 7, wherein the carbon fiber precursor fiber bundle (70A) has a surface processed with a pre-oxidation treatment in advance.

10. The carbon fiber manufacturing method as claimed in any one of the foregoing claims, wherein the resin oiling agent (80) is a thermosetting resin oiling agent.

11. The carbon fiber manufacturing method as claimed in any one of claims 1 to 9, wherein the resin oiling agent (80) is a thermoplastic resin oiling agent.

12. The carbon fiber manufacturing method as claimed in any one of the foregoing claims, wherein the carbon content of the carbon fiber (70B) is in the range of 80%-90%.

13. A carbon fiber manufacturing apparatus, comprising:

a feeding module (10) and a receiving module (20), the receiving module (20) being disposed in the vicinity of the feeding module (10), the feeding module (10) and the receiving module (20) constituting a carbon fiber drag route;

a high-temperature carbonization module (30), disposed at the carbon fiber drag route and located between the feeding module (10) and the receiving module (20) for heating the carbon fiber drag route;

a plasma surface treatment module (40), disposed at the carbon fiber drag route and located between the high-temperature carbonization module (30) and the receiving module (20) for supplying a plasma gas flow to the carbon fiber drag route; and

a sizing module (50), disposed at the carbon fiber drag route and located between the plasma surface treatment module (40) and the receiving module (20);

wherein the high-temperature carbonization module (30) has a chamber (31), a gas supply assembly (32), and a microwave generating assembly (33), the carbon fiber drag route passes through the chamber (31), the gas supply assembly (32) is used to supply an inert gas, and the microwave generating assembly (33) is used to supply a high-frequency microwave;

wherein the chamber (31) is a flat plate chamber and provided with at least one pair of microwave-sensitive materials (34)

14. The carbon fiber manufacturing apparatus as claimed in claim 13, wherein the plasma surface treatment module (40) is provided with at least one plasma generator (41).

15. The carbon fiber manufacturing apparatus as claimed in claim 13 or 14, wherein the plasma surface treatment module (40) is provided with at least one plasma generator (41) located at upper and lower positions of the carbon fiber drag route, respectively.

16. The carbon fiber manufacturing apparatus as claimed in any one of claims 13 to 15, wherein the chamber (31) is an elliptic chamber.

17. The carbon fiber manufacturing apparatus as claimed in any one of claims 13 to 16, wherein the chamber (31) is provided with at least one pair of microwave-sensitive materials (34).

18. The carbon fiber manufacturing apparatus as claimed in claim 14 or 15, wherein the plasma generator is able to generate the plasma gas flow, an atmospheric plasma gas flow, a low-pressure plasma gas flow, a microwave plasma gas flow, or a glow plasma gas flow having a power in the range of 100-10000 watts.

19. The carbon fiber manufacturing apparatus as claimed in any one of claims 13 to 18, wherein the sizing module (50) is provided with at least one reservoir (51).

20. The carbon fiber manufacturing apparatus as claimed in any one of claims 13 to 19, further comprising a drying module (60), the drying module (60) being disposed at the carbon fiber drag route between the sizing module (50) and the receiving module (20).

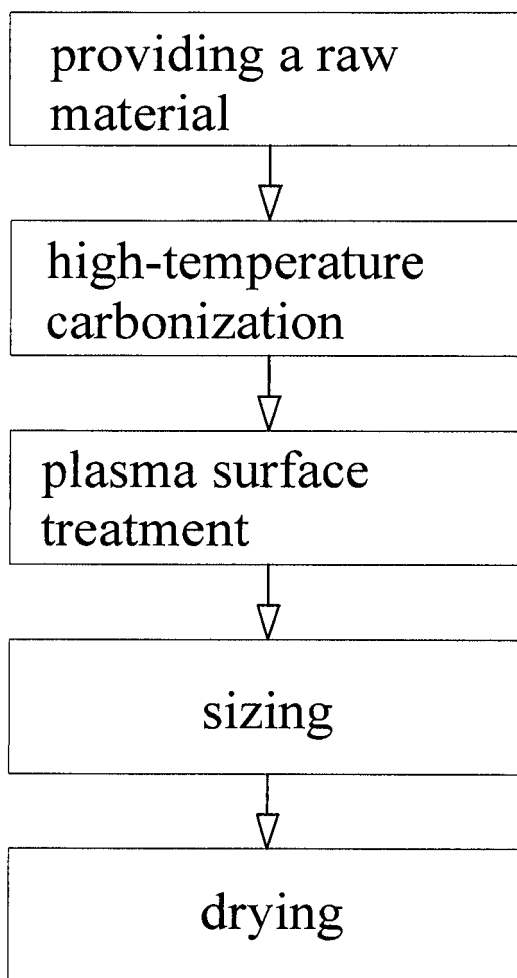


FIG.1

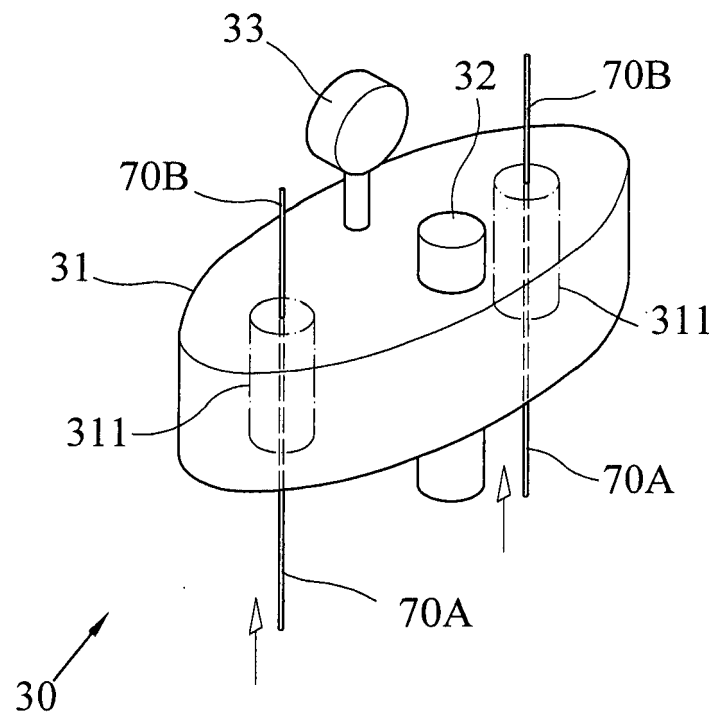


FIG.2

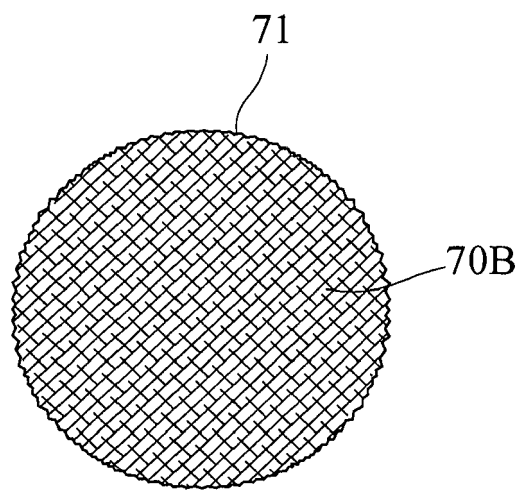


FIG.3

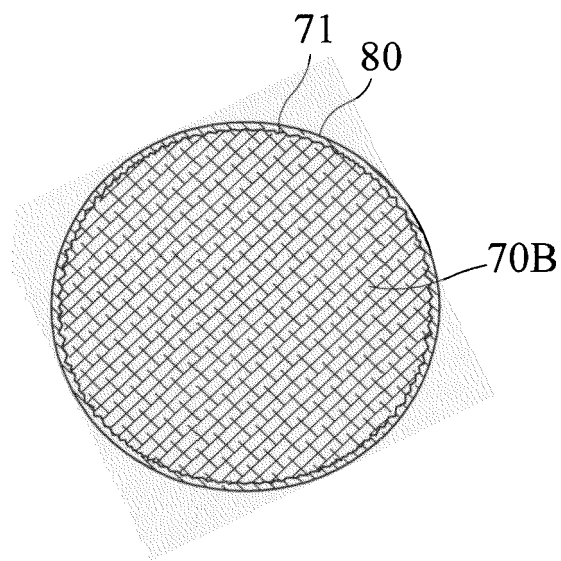


FIG.4

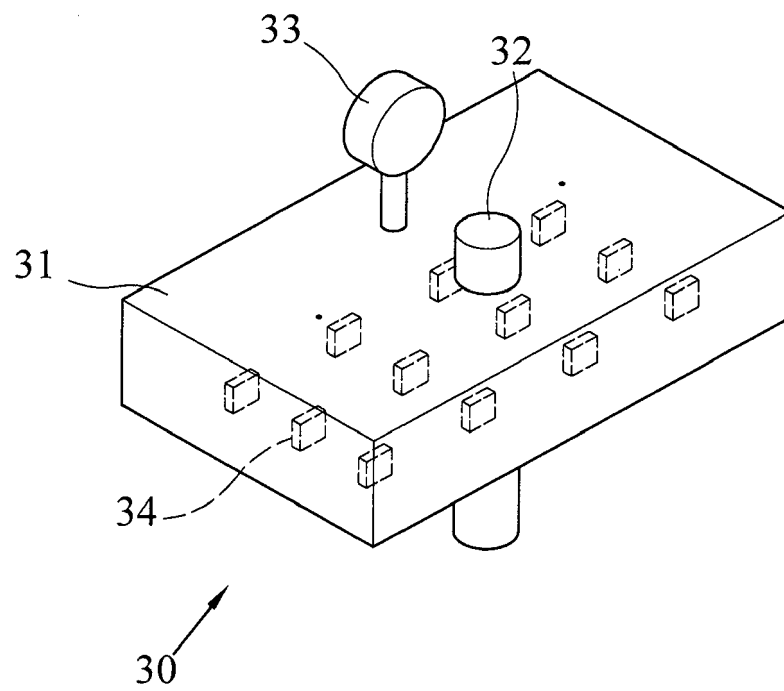


FIG.5

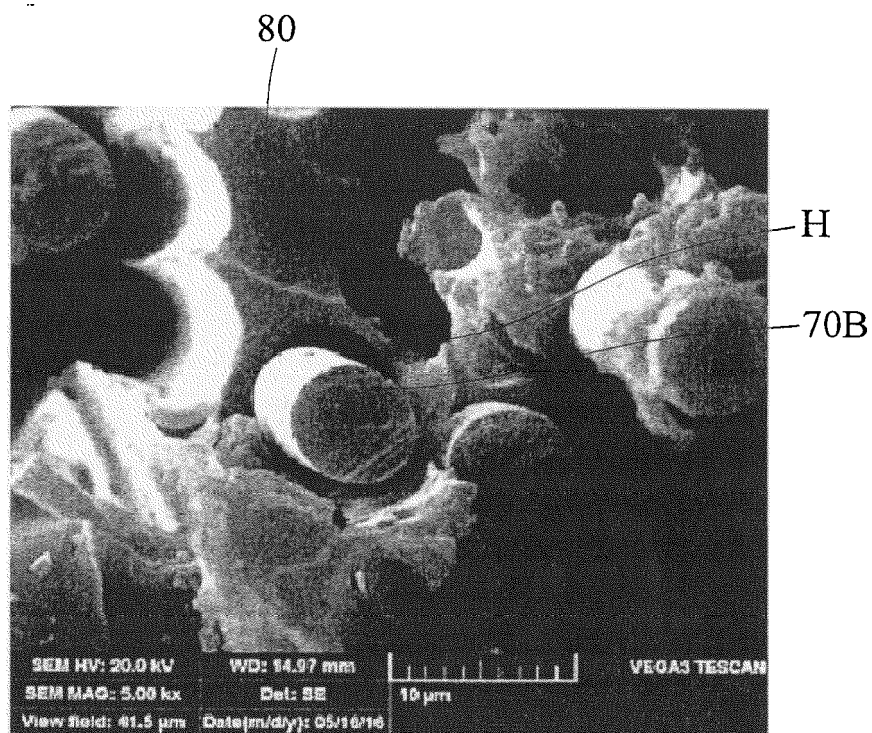


FIG.6a

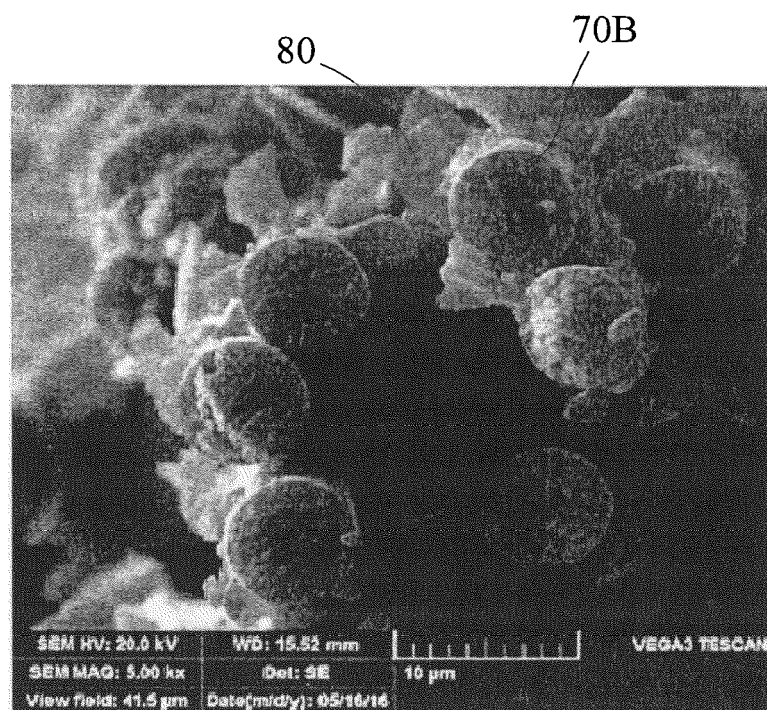


FIG.6b

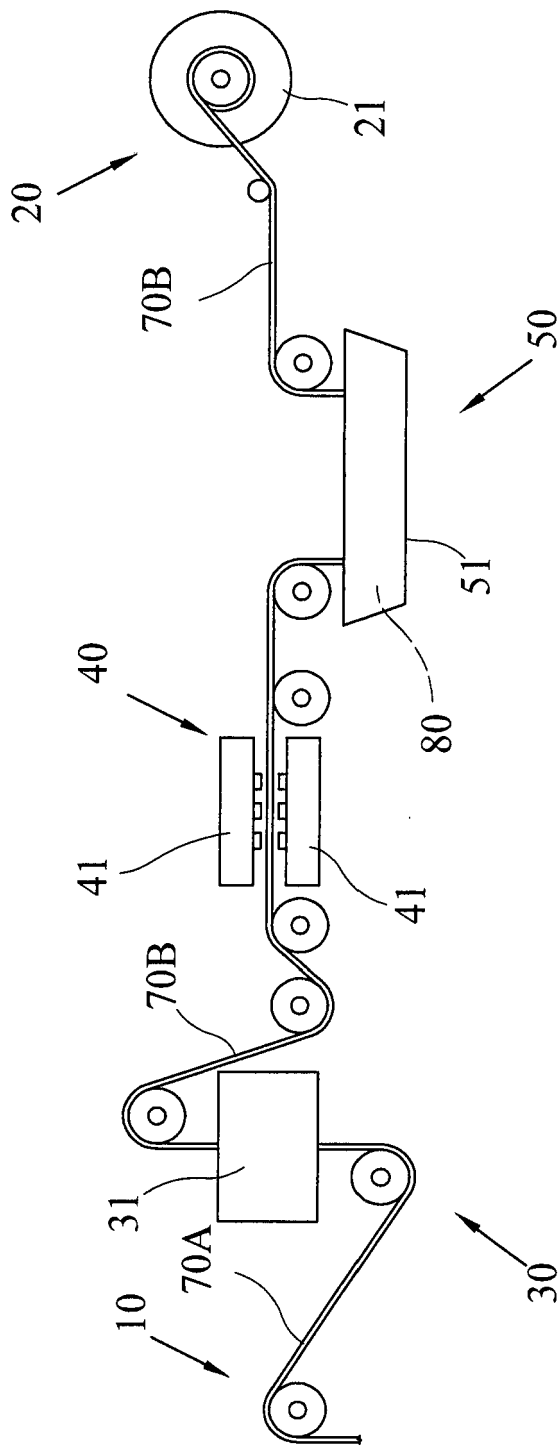


FIG.7

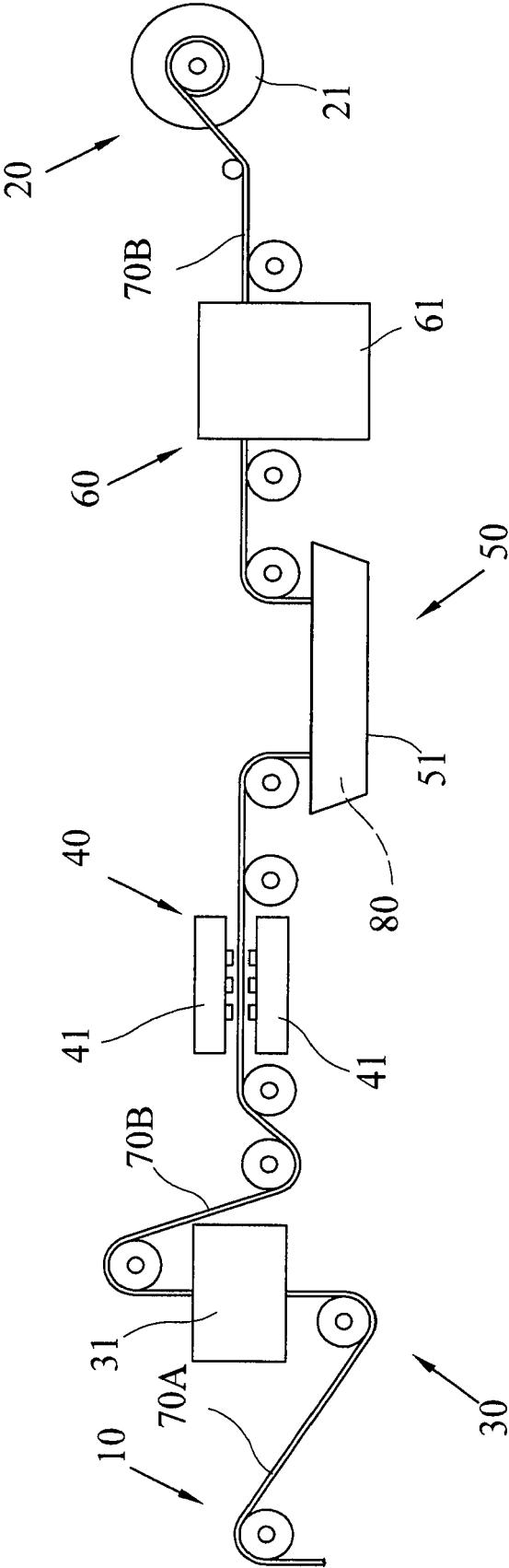


FIG.8



EUROPEAN SEARCH REPORT

Application Number
EP 17 00 0054

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2016/257797 A1 (VAUTARD FREDERIC [US] ET AL) 8 September 2016 (2016-09-08)	1,9-15, 24,25	INV.
A	* paragraphs [0003], [0008], [0011], [0020], [0021], [0040], [0050], [0051], [0052], [0056] *	2-8, 16-23	D01F9/22 D06M101/40
A	----- CN 104 342 936 A (UHT UNITECH CO LTD) 11 February 2015 (2015-02-11) * abstract *	1-25	

			TECHNICAL FIELDS SEARCHED (IPC)
			D01F D06M C08J
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 8 May 2017	Examiner Van Beurden-Hopkins
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 17 00 0054

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-05-2017

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016257797 A1	08-09-2016	US 2013224470 A1	29-08-2013
		US 2016257797 A1	08-09-2016
		US 2016311986 A1	27-10-2016
		US 2016312024 A1	27-10-2016
CN 104342936 A	11-02-2015	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82