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SURFACE MODIFICATION OF CARBON FIBERS

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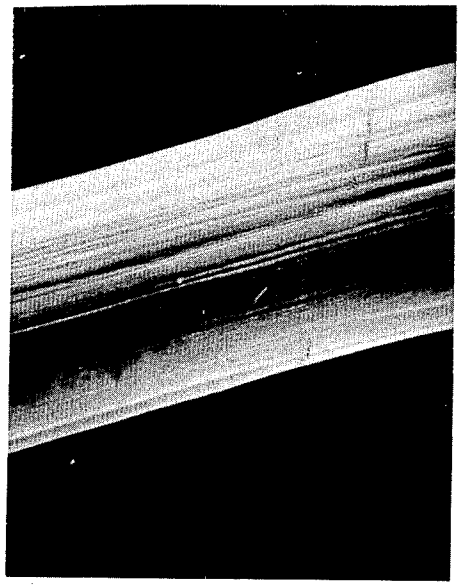
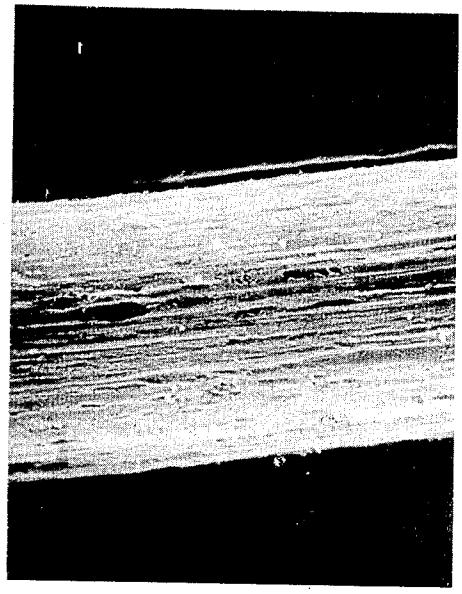


FIG. 1

FIG. 3



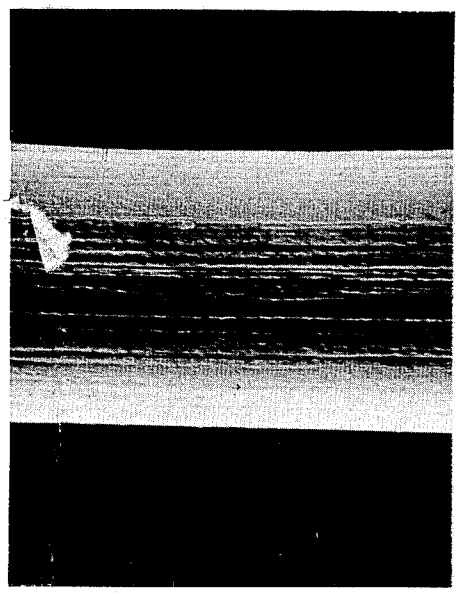


FIG. 2

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SURFACE MODIFICATION OF CARBON FIBERS

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ABSTRACT OF THE DISCLOSURE

A continuous process is provided for modifying the surface characteristics of a carbonaceous fibrous material (either amorphous carbon or graphitic carbon) and to thereby facilitate enhanced adhesion between the fibrous material and a matrix material. The fibrous material is continuously passed through a heating zone containing gaseous carbon dioxide under conditions found suitable for bringing about the desired surface modification. Composite articles of enhanced interlaminar shear strength may be formed by incorporating the fibers modified in accordance with the present process in a resinous matrix material.

BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon carbon fibers. The term "carbon fibers" is used herein in its generic sense and includes graphite fibers as well as amorphous carbon fibers. Graphite fibers are defined herein as fibers which consist essentially of carbon and have a predominant X-ray diffraction pattern characteristic of graphite. Amorphous carbon fibers, on the other hand, are defined as fibers in which the bulk of the fiber weight can be attributed to carbon and which exhibit an essentially amorphous X-ray diffraction pattern. Graphite fibers generally have a higher Young's modulus than do amorphous carbon fibers and in addition are more highly electrically and thermally conductive.

Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites, and carbon fibers theoretically have among the best properties of any fiber for use as high strength reinforcement. Among these desirable properties are corrosion and high temperature resistance, low density, high tensile strength, and high modulus. Graphite is one of the very few known materials whose tensile strength increases with temperature. Uses for carbon fiber reinforced composites include aerospace structural components, rocket motor casings, deep-submergence vessels and ablative materials for heat shields on re-entry vehicles.

In the prior art numerous materials have been proposed for use as possible matrices in which carbon fibers may be incorporated to provide reinforcement and produce a composite article. The matrix material which is selected is commonly a thermosetting resinous material and is commonly selected because of its ability to also withstand highly elevated temperatures.

While it has been possible in the past to provide carbon fibers of highly desirable strength and modulus characteristics, difficulties have arisen when one attempts to gain the full advantage of such properties in the resulting carbon fiber reinforced composite article. Such inability to capitalize upon the superior single filament properties of the reinforcing fiber has been traced to inadequate adhesion between the fiber and the matrix in the resulting composite article.

Various techniques have been proposed in the past for modifying the fiber properties of a previously formed carbon fiber in order to make possible improved adhesion when present in a composite article. See, for instance,

British Pat. No. 1,180,441 to Nicholas J. Wadsworth and William Watt wherein it is taught to heat a carbon fiber normally within the range of 350° C. to 850° C. (e.g. 500 to 600° C.) in an oxidizing atmosphere such as air for an appreciable period of time. Other atmospheres contemplated for use in the process include an oxygen rich atmosphere, pure oxygen, or an atmosphere containing an oxide of ntirogen from which free oxygen becomes available such as nitrous oxide and nitrogen dioxide.

It is an object of the invention to provide a continuous process for efficiently modifying the surface characteristics of carbon fibers.

It is an object of the invention to provide a process for improving the ability of carbon fibers to bond to a resinous matrix material.

It is an object of the invention to provide a process for modifying the surface characteristics of carbon fibers which may be conducted relatively rapidly.

It is another object of the invention to provide composite articles reinforced with carbon fibers exhibiting improved interlaminar shear strength.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF THE INVENTION

It has been found that a process for the modification of the surface characteristics of a carbonaceous fibrous material containing at least about 90 percent carbon by weight comprises continuously passing a continuous length of said fibrous material through a heating zone provided at a temperature of about 700 to 1800° C. containing a gaseous atmosphere consisting essentially of about 0.5 to 100 percent by volume of carbon dioxide and about 0 to 99.5 percent by volume of an inert gas for a residence time of about 3 seconds to 1 hour.

The resulting carbon fibers may be incorporated in a resinous matrix material to form a composite article exhibiting enhanced interlaminar shear strength.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph made with the aid of a scanning electron microscope of a portion of graphite filament which has not undergone surface modification.

FIG. 2 is a photograph made with the aid of a scanning electron microscope of a portion of a graphite filament which has been surface modified in accordance with the present process.

FIG. 3 is a photograph made with the aid of a scanning electron microscope of a portion of a graphite filament which has undergone surface modification while employing other than optimum surface treatment conditions.

DESCRIPTION OF PREFERRED EMBODIMENTS

The starting material

The fibers which are modified in accordance with the present process are carbonaceous and contain at least about 90 percent carbon by weight. Such carbon fibers may exhibit either an amorphous carbon or a predominantly graphitic carbon X-ray diffraction pattern. In a preferred embodiment of the process the carbonaceous fibers which undergo surface treatment contain at least about 95 percent carbon by weight, and at least about 99 percent carbon by weight in a particularly preferred embodiment of the process.

The carbonaceous fibrous materials may be present as a continuous length in a variety of physical configurations provided substantial access to the fiber surface is possi-

ble during the surface modification treatment described hereafter. For instance, the carbonaceous fibrous materials may assume the configuration of a continuous length of a multifilament yarn, tape, tow, strand, cable, or similar fibrous assemblage. In a preferred embodiment of the process the carbonaceous fibrous material is one or more continuous multifilament yarn. When a plurality of multifilament yarns are surface treated simultaneously, they may be continuously passed through the heating zone while in parallel and in the form of a flat ribbon.

The carbonaceous fibrous material which is treated in the present process optionally may be provided with a twist which tends to improve the handling characteristics. For instance, a twist of about 0.1 to 5 t.p.i., and preferably about 0.3 to 1.0 t.p.i., may be imparted to a multifilament yarn. Also, a false twist may be used instead of or in addition to a real twist. Alternatively, one may select continuous bundles of fibrous material which possess essentially no twist.

The carbonaceous fibers which serve as the starting material in the present process may be formed in accordance with a variety of techniques as will be apparent to those skilled in the art. For instance, organic polymeric fibrous materials which are capable of undergoing thermal stabilization may be initially stabilized by treatment in an appropriate atmosphere at a moderate temperature (e.g. 200 to 400° C.), and subsequently heated in an inert atmosphere at a more highly elevated temperature, e.g. 900 to 1000° C., or more, until a carbonaceous fibrous material is formed. If the thermally stabilized material is heated to a maximum temperature of 2000 to 3100° C. (preferably 2400 to 3100° C.) in an inert atmosphere, substantial amounts of graphitic carbon are commonly detected in the resulting carbon fiber, otherwise the carbon fiber will commonly exhibit an essentially amorphous X-ray diffraction pattern.

The exact temperature and atmosphere utilized during the initial stabilization of an organic polymeric fibrous material commonly vary with the composition of the precursor as will be apparent to those skilled in the art. During the carbonization reaction elements present in the fibrous material other than carbon (e.g. oxygen and hydrogen) are substantially expelled. Suitable organic polymeric fibrous materials from which the fibrous material capable of undergoing carbonization may be derived include an acrylic polymer, a cellulosic polymer, a polyamide, a polybenzimidazole, polyvinyl alcohol, etc. As discussed hereafter, acrylic polymeric materials are particularly suited for use as precursors in the formation of carbonaceous fibrous materials. Illustrative examples of suitable cellulosic materials include the natural and regenerated forms of cellulose, e.g. rayon. Illustrative examples of suitable polyamide materials include the aromatic polyamides, such as nylon 6T, which is formed by the condensation of hexamethylenediamine and terephthalic acid. An illustrative example of a suitable polybenzimidazole is poly-2,2′-m-phenylene-5,5′-bibenzimidazole.

A fibrous acrylic polymeric material prior to stabilization may be formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should contain not less than about 85 mole percent of recurring acrylonitrile units with not more than about 15 mole percent of a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monovinyl compounds.

During the formation of a preferred carbonaceous fibrous material for use in the present process multifilament bundles of an acrylic fibrous material may be initially stabilized in an oxygen-containing atmosphere (i.e. preoxidized) on a continuous basis in accordance with the teachings of U.S. Ser. No. 749,957, filed Aug. 5, 1968, of Dagobert E. Stuetz, which is assigned to the same assignee as the present invention and is herein incorporated by reference. More specifically, the acrylic fibrous material should be either an acrylonitrile homopolymer or an acrylonitrile copolymer which contains no more than about 5 mole percent of one or more monovinyl comonomers copolymerized with acrylonitrile. In a particularly preferred embodiment of the process the fibrous material is derived from an acrylonitrile homopolymer. The stabilized acrylic fibrous material which is preoxidized in an oxygen-containing atmosphere is black in appearance, contains a bound oxygen content of at least about 7 percent by weight as determined by the Unterzaucher analysis, retains its original fibrous configuration essentially intact, and is non-burning when subjected to an ordinary match flame.

In preferred techniques for forming the starting material for the present process a stabilized acrylic fibrous material is carbonized and graphitized while passing through a temperature gradient present in a heating zone in accordance with the procedures described in commonly assigned U.S. Ser. Nos. 777,275, filed Nov. 20, 1968 of Charles M. Clarke; 17,780, filed Mar. 9, 1970 of Charles M. Clarke, Michael J. Ram, and John P. Riggs; and 17,832, filed Mar. 9, 1970 of Charles M. Clarke, Michael J. Ram, and Arnold J. Rosenthal. Each of these disclosures is herein incorporated by reference.

In accordance with a particularly preferred carbonization and graphitization technique a continuous length of stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mole percent of acrylonitrile units and up to about 15 mole percent of one or more monovinyl units copolymerized therewith is converted to a graphitic fibrous material while preserving the original fibrous configuration essentially intact while passing through a carbonization/graphitization heating zone containing an inert gaseous atmosphere and a temperature gradient in which the fibrous material is raised within a period of about 20 to about 300 seconds from about 800° C. to a temperature of about 1600° C. to form a continuous length of carbonized fibrous material, and in which the carbonized fibrous material is subsequently raised from about 1600° C. to a maximum temperature of at least about 2400° C. within a period of about 3 to 300 seconds where it is maintained for about 10 seconds to about 200 seconds to form a continuous length of graphitic fibrous material.

The equipment utilized to produce the heating zone used to produce the carbonaceous starting material may be varied as will be apparent to those skilled in the art. It is essential that the apparatus selected be capable of producing the required temperature while excluding the presence of an oxidizing atmosphere.

In a preferred technique the continuous length of fibrous material undergoing carbonization is heated by use of an induction furnace. In such a procedure the fibrous material may be passed in the direction of its length through a hollow graphite tube or other susceptor which is situated within the windings of an induction coil. By varying the length of the graphite tube, the length of the induction coil, and the rate at which the fibrous material is passed through the graphite tube, many apparatus arrangements capable of producing carbonization or carbonization and graphitization may be selected. For large scale production, it is of course preferred that relatively long tubes or susceptors be used so that the fibrous material may be passed through the same at a more rapid rate while being carbonized or carbonized and graphitized. The temperature gradient of a given apparatus may be determined by conventional optical pyrometer measurements as will be apparent to those skilled in the art. The fibrous material because of its small mass and relatively large surface area instanta-

neously assumes essentially the same temperature as that of the zone through which it is continuously passed.

The surface treatment

The continuous length of carbonaceous fibrous material is continuously passed (e.g. in the direction of its length) through a heating zone containing a gaseous atmosphere consisting essentially of about 0.5 to 100 percent by volume of carbon dioxide (preferably 5 to 100 percent by volume carbon dioxide) and about 0 to 99.5 percent by volume of an inert carrier gas (preferably 0 to 95 percent by volume inert carrier gas) under the conditions described in detail hereafter. Suitable inert carrier gases include nitrogen, argon, and helium, etc. In a particularly preferred embodiment of the process the gaseous atmosphere of the heating zone is essentially pure carbon dioxide thereby eliminating the need to supply more than one gas to the heating zone as well as the difficulties connected with the feeding of a plurality of gases to produce a gaseous mixture of the desired concentration. It is recommended that molecular oxygen be excluded from the heating zone, however, trace amounts of molecular oxygen (e.g. up to about 2 perecnt by volume) can generally be tolerated in combination with the active carbon dioxide species without deleterious results.

The gaseous atmosphere (heretofore described) is provided in the heating zone at a temperature of about 700 to 1800° C. At temperatures much below about 700° C. the surface treatment reaction tends to be inordinately slow. At temperatures much above about 1800° C. the surface treatment reaction becomes so rapid that it is difficult to control. If desired a temperature gradient may be provided within the heating zone which rises to the desired surface treatment temperature. The gaseous atmosphere preferably is preheated prior to introduction into the heating zone and preferably is continuously supplied to the heating zone with a portion of the gaseous atmosphere being continuously withdrawn from the heating zone whereby off gases are effectively expelled. In a preferred embodiment of the process wherein the gaseous atmosphere is essentially pure carbon dioxide the gaseous atmosphere is provided at a temperature of about 900 to 1300° C.

The contact time during which the carbonaceous fibrous material is passed through the heating zone commonly ranges from about 3 seconds to 1 hour. The minimum contact time varies with the concentration of carbon dioxide in the gaseous atmosphere, the temperature of the gaseous atmosphere, and the relative molar concentrations of carbon dioxide and carbon present in the carbonaceous fibrous material within the heating zone. Generally the higher the temperature of the carbon dioxide containing gaseous atmosphere, the more rapid the surface modification. Generally the higher the concentration of carbon dioxide in the gaseous atmosphere, the more rapid the surface modification. Also it has been observed that graphitic fibrous materials of high Young's modulus (e.g. in excess of 50,000,000 p.s.i.) tend to require a slightly longer contact time for optimum results than do carbonaceous fibrous materials of a predominantly amorphous X-ray diffraction pattern which generally exhibit a lower Young's modulus. Also when the carbonaceous fibrous material is provided as a relatively compact assemblage of a plurality of fibers, then longer residence times may be advantageously employed as will be apparent to those skilled in the art.

The surface modification treatment of the present process is generally terminated prior to achieving a fiber weight loss much in excess of 10 percent by weight. Greater fiber weight losses are to be avoided since such weight losses are generally indicative of an excessive surface treatment and yield no commensurate advantage. In fact, the effectiveness of the surface treatment previously achieved may actually be diminished in some instances. Fiber weight losses of about 0.5 to 7 percent by weight (e.g. 1 or 2 percent by weight) are commonly attained in particularly preferred embodiments of the present process.

A particularly preferred embodiment of the present process for the modification of the surface characteristics of a carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern comprises: (a) continuously introducing a continuous length of the fibrous material into a heating zone provided at a temperature of about 900 to 1300° C. containing a gaseous carbon dioxide atmosphere, (b) continuously introducing essentially pure gaseous carbon dioxide into said heating zone, (c) continuously withdrawing a portion of the gaseous atmosphere from said heating zone, (d) continuously passing said continuous length of carbonaceous fibrous material through said heating zone at said temperature for a residence time of about 3 to 240 seconds, and (e) continuously withdrawing the resulting continuous length of carbonaceous fibrous material from said heating zone.

The theory whereby the surface of a carbonaceous fibrous material is modified in the present process is considered complex and incapable of simple explanation. It is believed, however, that the resulting modification is attributable to a combination of physical and chemical interactions between the gaseous atmosphere and the carbonaceous fibrous material. Such interaction likely includes the chemical reaction of carbon dioxide with carbon adjacent the surface of the fiber to yield carbon monoxide. Such carbon monoxide may be continuously withdrawn from the heating zone together with any other off gases which are evolved.

The surface modification imparted to the carbonaceous fibrous material through the use of the present process has been found to exhibit an appreciable life which is not diminished to any substantial degree even after the passage of 30, or more days.

The surface treatment of the present process makes possible improved adhesive bonding between the carbonaceous fibers, and a resinous matrix material. Accordingly, carbon fiber reinforced composite materials which incorporate fibers treated as heretofore described exhibit enhanced shear strength, flexural strength, compressive strength, etc. The resinous matrix material employed in the formation of such composite materials is commonly a polar thermosetting resin such as an epoxy, a polyimide, a polyester, a phenolic, etc. The carbonaceous fibrous material is commonly provided in such resulting composite materials in either an aligned or random fashion in a concentration of about 20 to 70 percent by volume.

The following examples are given as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

EXAMPLE I

A high strength-high modulus carbonaceous yarn derived from an acrylonitrile homopolymer yarn in accordance with procedures described in U.S. Ser. No. 749,957, filed Aug. 5, 1968, and 777,275 filed Nov. 20, 1968 was selected as the starting material. The yarn consisted of a 1600 fil. bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 358,000 p.s.i., and a single filament Young's modulus of about 115,000,000 p.s.i. A photograph of a filament of the untreated yarn made with the aid of a scanning electron microscope at a magnification of 6400× is provided as FIG. 1.

Portions of the yarn were continuously unwound from bobbins and 15 ends of the yarn were continuously passed while in parallel and in the form of a flat ribbon at various rates through a heat treatment zone provided with a tem-

perature gradient containing an atmosphere of essentially pure carbon dioxide.

The heat treatment zone consisted of an 18 inch Inconel tube having an inner diameter of about 1 inch which was positioned within a resistance wound muffle furnace having a length of 12 inches. Three inches of the Inconel tube protruded from each end of the muffle furnace. A hot zone (maximum temperature portion of gradient) having a length of about 3 inches was centrally located in the Inconel tube through which the yarn continuously passed and was adjusted to a constant temperature of about 1050° C.

Gaseous carbon dioxide was continuously introduced into the Inconel tube at the yarn feed end at a rate of 25 s.c.f.h. (std. cu. ft. per hour). Air was excluded from the heat treatment zone by means of a nitrogen padded chamber which enclosed the surface treatment chamber. Off gases were continuously displaced and withdrawn from the heat treatment zone by the continuously introduced gas supply. Off gases were withdrawn from the surface treatment zone primarily at the yarn exit end of the tube. The fiber weight losses which occurred during the surface treatment were less than 10 percent, e.g. commonly 1 to 3 percent.

Composite articles were next formed employing the surface modified yarn samples as a reinforcing medium in a resinous matrix. The composite articles were rectangular bars consisting of about 50 percent by volume of the yarn and having dimensions of ⅛ inch x ¼ inch x 5 inches. The composite articles were formed by impregnation of the yarn in a liquid epoxy resin-hardener mixture at 50° C. followed by unidirectional layup of the required quantity of the impregnated yarn in a steel mold and compression molding of the layup for 2 hours at 93° C., and 2.5 hours at 200° C. in a heated platen press at about 100 p.s.i. pressure. The mold was cooled slowly to room temperature, and the composite article was removed from the mold cavity and cut to size for testing. The resinous matrix material used in the formation of the composite article was provided as a solventless system which contained 100 parts by weight of epoxy resin and 88 parts by weight of anhydride curing agent.

The following data summarizes the surface treatment conditions employed and the properties achieved.

Sample	Yarn speed, in./min.	Time at 1,050° C. in seconds	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	10	15	348,000	6,160
B	5	30	340,000	6,790
C	2.5	60	325,000	9,060
D	1	150	287,000	9,500

The horizontal interlaminar shear strengths reported were determined by short beam testing of the carbon fiber reinforced composite according to the procedure of ASTM D2344–65T as modified for straight bar testing at a 4:1 span to depth ratio.

For comparative purposes a composite article was formed as heretofore described employing an identical carbonaceous yarn without subjecting the same to any form of surface modification. The average horizontal interlaminar shear strength of the composite article was only 3000 p.s.i.

A photograph of a filament of the surface treated yarn of Sample C (above) made with the aid of a scanning electron microscope at a magnification of 6400× is provided as FIG. 2.

EXAMPLE II

Example I was repeated with the exception that the three inch hot zone of the Inconel tube was provided at a temperature of 1135° C.

The following data summarizes the surface treatment conditions employed and the properties achieved.

Sample	Yarn speed, in./min.	Time at 1,050° C. in seconds	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	10	15	332,000	7,950
B	5	30	269,000	9,615
C	2.5	60	230,000	8,860
D	1.5	100	230,000	7,715

EXAMPLE III

Example I was repeated with the exception that the three inch hot zone of the Inconel tube was provided at a temperature of 1250° C.

The following data summarizes the surface treatment conditions employed and the properties achieved.

Sample	Yarn speed, in./min.	Time at 1,050° C. in seconds	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	40	3.75	269,000	9,035
B	20	7.5	246,000	9,080
C	10	15	230,000	8,860
D	5	30	230,000	7,860
E	2.5	60	205,000	6,570

A comparison of the properties achieved indicates that Sample E received more than the optimum degree of surface treatment. Additionally a fiber weight loss of about 20 percent was experienced in Sample E. A photograph of a filament of the surface treated yarn made with the aid of a scanning electron microscope at a magnification of 6600× is provided as FIG. 3.

EXAMPLE IV

A high strength-high modulus yarn substantially similar to that employed in Examples I–III was selected as the starting material. The yarn consisted of a 1600 fil bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphic X-ray diffraction pattern, a single filament tenacity of 302,000 p.s.i., and a single filament Young's modulus of about 87,000,000 p.s.i.

Portions of the yarn were surface treated and formed into composites as described in Example I.

The following data summarizes the surface treatment conditions employed and the properties achieved when the hot zone of the Inconel tube was provided at 900° C.

Sample	Yarn speed, in./min.	Time at 900° C. in seconds	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	10	15	302,000	5,980
B	5	30	256,000	10,800
C	2.5	60	210,000	10,850
D	1.25	120	177,000	10,100

EXAMPLE V

A high strength-high modulus yarn substantially similar to that employed in Examples I–IV was selected as the starting material. The yarn consisted of a 1600 fil bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 281,000 p.s.i., and a single filament Young's modulus of 87,000,000 p.s.i.

Portions of the yarn were surface treated and formed into composites as described in Example I.

The following data summarizes the surface treatment conditions employed and the properties achieved when the hot zone of the Inconel tube was provided at 1050° C.

Sample	Yarn speed, in./min.	Time at 1,050° C. in seconds	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	10	15	204,000	10,350
B	2.5	60	175,000	7,715

A comparison of the properties achieved indicates that Sample B received more than the optimum degree of surface treatment. Additionally, a fiber weight loss of 22 percent was experienced in Sample B, while a weight loss of only 7.5 percent was experienced in Sample A.

For comparative purposes the surface treatment of a carbonaceous fiber was attempted employing essentially pure carbon monoxide in the heating zone. The bonding characteristics of the fiber to a matrix material were not enhanced.

EXAMPLE VI

A high strength-high modulus yarn substantially similar to that employed in Examples I–V was selected as the starting material. The yarn consisted of a 1600 fil bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 340,000 p.s.i., and a single filament Young's modulus of about 90,000,000 p.s.i.

Portions of the yarn were surface treated and formed into composites as described in Example I with the exception that a premixed gaseous mixture of carbon dioxide and nitrogen was utilized in the heating zone.

The following data summarizes the surface treatment conditions employed and the properties achieved when the hot zone of the Inconel tube was provided at 1280° C.

Sample	Yarn speed, in./min.	Time at 1,280° C. seconds	Volume percent CO_2 in mixture	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	10	15	7.4	282,000	7,065
B	10	15	16.0	272,000	10,345
C	10	15	33.0	300,000	10,290

EXAMPLE VII

Example VI was repeated employing a substantially similar high strength-high modulus yarn, and a different apparatus capable of producing a temperature gradient having a 10 inch hot zone at a temperature of about 1700° C.

The yarn consisted of a 1600 fil bundle having a total denier of about 1000, had a carbon content in excess of 99 percent by weight, exhibited a predominantly graphitic X-ray diffraction pattern, a single filament tenacity of about 326,000 p.s.i., and a single filament Young's modulus of about 90,000,000 p.s.i.

The heat treatment zone consisted of a 48 inch long ceramic tube having an inner diameter of about 0.5 inch which was positioned within a graphite susceptor of an indication furnace having a length of 42 inches.

The premixed gaseous atmosphere was continuously introduced into the yarn feed end of the ceramic tube at a rate of 25.0 s.c.f.h. Air was excluded from the heat treatment zone by means of a nitrogen padded chamber which enclosed the heat treatment furnace. Off gases were continuously displaced and withdrawn from the heat treatment zone by the continuously introduced gas supply. Off gases were withdrawn from the surface treatment zone primarily at the yarn exit end of the tube.

Portions of the yarn were surface treated and formed into composites as previously described.

The following data summarizes the surface treatment conditions employed and the properties achieved when the hot zone of the ceramic tube was provided at 1700° C.

Sample	Yarn speed, in./min.	Time at 1700° C. seconds	Volume percent CO_2 in mixture	Single filament tenacity after surface treatment, p.s.i.	Interlaminar shear strength of composite, p.s.i.
A	30	20	0.4	325,000	5,330
B	30	20	0.8	320,000	5,695
C	30	20	3.2	294,000	9,365

The resulting surface modified carbonaceous fiber may next be utilized as a reinforcing medium in the formation composite articles by incorporation in a resinous matrix material.

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. An improved process for the modification of the surface characteristics of a carbonaceous fibrous material containing at least about 95 percent carbon by weight and exhibiting a predominantly graphitic X-ray diffraction pattern so as to improve its ability to bond to a resinous matrix material comprising:

(a) continuously introducing a continuous length of said carbonaceous fibrous material into a heating zone provided at a temperature of about 900 to 1300° C. containing a gaseous carbon dioxide atmosphere,

(b) continuously introducing essentially pure gaseous carbon dioxide into said heating zone,

(c) continuously withdrawing a portion of the gaseous atmosphere from said heating zone,

(d) continuously passing said continuous length of said carbonaceous fibrous material in the direction of its length through said heating zone at said temperature for a residence time of about 3 to 240 seconds, and

(e) continuously withdrawing the resulting continuous length of carbonaceous fibrous material from said heating zone.

2. An improved process according to claim 1 wherein said carbonaceous fibrous material contains at least about 99 percent carbon by weight.

3. An improved process according to claim 1 wherein said carbonaceous fibrous material is derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mole percent of acrylonitrile units and up to about 15 mole percent of one or more monovinyl units copolymerized therewith.

4. An improved process according to claim 1 wherein said continuous length of carbonaceous fibrous material is one or more continuous multifilament yarn.

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JAMES E. POER, Primary Examiner

U.S. Cl. X.R.

23—209.1, 209.2