

[54] **PROCESS FOR THE PRODUCTION OF
LARGE DENIER CARBON FIBERS**

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[51] Int. Cl. **C01b 31/07**

[58] Field of Search **423/447; 264/29**

[56] **References Cited**

UNITED STATES PATENTS

3,305,315	2/1967	Bacon et al.	423/447
3,449,077	6/1969	Stuetz	423/447
3,528,774	9/1970	Ezekiel et al.	423/447
3,595,946	7/1971	Joo et al.	423/447 X
3,634,035	1/1972	Stuetz	423/447
3,635,675	1/1972	Ezekiel	423/447
3,656,910	4/1972	Ferment	423/447 X

3,666,417	5/1972	Araki et al.	423/447
3,720,759	3/1973	Overhoff	423/447

FOREIGN PATENTS OR APPLICATIONS

47-26974	7/1972	Japan	423/447
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[57] **ABSTRACT**

An improved process is provided for the expeditious formation of large denier carbon fibers, i.e. carbon fibers having a single filament denier of at least 30. A fibrous polybenzimidazole starting material of relatively large denier is initially converted to a polybenzimidazonium salt by contact with a solution of certain acids at an elevated temperature, and the resulting fibrous material sequentially is heated in oxygen-containing and non-oxidizing gaseous atmospheres at successively elevated temperatures. The resulting carbonaceous fibrous material contains at least 90 percent carbon by weight and particularly is suited for use as a reinforcing medium in a matrix material, e.g. either a polymeric or metallic matrix material.

18 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF LARGE DENIER CARBON FIBERS

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.

As is well known to those skilled in the art, carbon fibers commonly have been formed by the thermal stabilization of a variety of polymeric fibrous materials, and the subsequent carbonization or carbonization and graphitization of the same in an inert atmosphere. Representative U.S. patents disclosing the production of carbon fibers from an acrylic fibrous precursor include: U.S. Pat. Nos. 2,913,802; 3,285,696; 3,539,295; 3,592,595; 3,647,770; 3,650,668; 3,656,882; 3,656,883; 3,708,326; and 3,729,549. Representative U.S. patents disclosing the production of carbon fibers from a polybenzimidazole fibrous material include: U.S. Pat. Nos. 3,449,077; 3,528,774; 3,634,035; and 3,635,675.

Heretofore, the carbon fibers produced in the prior art have tended to have a relatively small denier per filament, e.g. about 0.5 to 2.0 denier per filament corresponding to an average filament diameter of about 0.0003 to 0.0005 inches. Whenever attempts have been made to produce carbon fibers of relative large denier per filament, e.g. 30 to 400 or more, and a filament diameter of 0.001 inch or more special problems have been presented particularly during the stabilization portion of the process. It has been recognized that unless the polymeric fibrous precursor is adequately stabilized (e.g. by heating in air or other oxidizing atmosphere), it cannot be satisfactorily carbonized or carbonized and graphitized. During the stabilization portion of the process it has been found that an oxidized surface layer tends initially to form upon the fiber surface which tends to impede oxygen diffusion into the fiber and to retard the further stabilization thereof. Accordingly extremely long stabilization periods have been required when the fibrous precursor is a relatively large denier per filament. Additionally, the subsequent carbonization treatment of the resulting stabilized fibrous material has tended to be slow.

Commonly assigned U.S. Ser. No. 296,725, filed Oct. 11, 1972, now abandoned, of John W. Soehngen discloses an approach for lessening the time required for the stabilization of an acrylic fibrous precursor of larger than usual diameter.

Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites wherein carbon fibers are incorporated in a resinous or metallic matrix. 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 tem-

perature 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 recreational equipment, such as golf club shafts, aerospace structural components, rocket motor casings, deep-submergence vessels, ablative materials for heat shields on re-entry vehicles, etc.

There has remained a need for improved techniques to produce carbon fibers of a relatively large denier which are derived from a polymeric fibrous material of relatively large denier. Such large denier carbon fibers are capable, inter alia, of forming composite articles exhibiting an enhanced compressive strength to tensile strength ratio. Also, such large denier carbon fibers are particularly suited for use as fibrous reinforcement in a metallic matrix. When one attempts to incorporate a relatively small diameter carbon filament in a metallic matrix, it has been observed that the outer portion of the filament tends to react with the matrix during composite fabrication which results in a loss of most of the filament strength. Accordingly, commercially practicable processes for producing large denier carbon filaments are in demand, but have proven to be an elusive goal.

It is an object of the invention to provide an improved process for the production of large denier carbon fibers.

It is an object of the invention to provide an improved process for the production of large denier carbon fibers beginning with large denier polybenzimidazole fibrous precursors.

It is an object of the invention to provide a process for the production of large denier carbon fibers beginning with a large denier polybenzimidazole fibrous precursor wherein the stabilization portion thereof is carried out on an expeditious basis without the necessity to employ extremely long residence times as commonly required in the prior art thereby yielding improved production efficiency.

It is another object of the invention to provide large denier carbon filaments which may be readily substituted for boron filaments as reinforcement in a metallic matrix.

It is another object of the invention to provide large denier carbon filaments which may be used as a substrate for receiving the vapor deposition of boron to form a boron-carbon composite fiber suitable for incorporation in a metallic matrix.

It is a further object of the invention to provide an improved process for the production of large denier carbon fibers in which the various thermal processing steps thereof expeditiously may be carried out in an inline continuous manner.

These and other objects, as well as, the scope, nature, and utilization of the process will be apparent to those skilled in the art from the following description and appended claims.

SUMMARY OF THE INVENTION

It has been found that an improved process for the formation of a large denier carbonaceous fibrous material comprises:

- a. contacting a polybenzimidazole fibrous material having a denier per filament of about 50 to 600 with a solution of an acid having a pK_A value below about 4.5 while at an elevated temperature to transform

Any polymerization process known to those skilled in the art may be employed to prepare the polybenzimidazole which may then be formed into a continuous length of fibrous material. Representative techniques for preparing the polybenzimidazole are disclosed in U.S. Pat. Nos. 3,509,108; 3,549,603; and 3,551,389, which are assigned to the assignee of the present invention and are herein incorporated by reference.

With respect to aromatic polybenzimidazoles, preferably equimolar quantities of the monomeric tetraamine and dicarboxyl compound are introduced into a first stage melt polymerization reaction zone and heated therein at a temperature above about 200°C., preferably at least 250°C., and more preferably from about 270° to 300°C. The reaction is conducted in a substantially oxygen-free atmosphere, i.e., below about 20 ppm oxygen and preferably below about 8 ppm oxygen, until a foamed prepolymer is formed having an inherent viscosity, expressed as deciliters per gram, of at least 0.1 and preferably from about 0.13 to 0.3, the inherent viscosity (I.V.) as used herein being determined from a solution of 0.4 grams of the polymer in 100 ml. of 97 percent H₂SO₄ at 25°C.

After the conclusion of the first stage reaction, which normally takes at least 0.5 hour and preferably 1 to 3 hours, the foamed prepolymer is cooled and then powdered or pulverized in any convenient manner. The resulting prepolymer powder is then introduced into a second stage polymerization reaction zone wherein it is heated under substantially oxygen-free conditions, as described above, to yield a polybenzimidazole polymer product, desirably having an I.V., as measured above, of at least 0.6, e.g., 0.80 to 1.1 or more.

The temperature employed in the second stage is at least 250°C., preferably at least 325°C., and more preferably from about 350° to 425°C. The second stage reaction generally takes at least 0.5 hour, and preferably from about 1 to 4 hours or more.

A particularly preferred method for preparing the polybenzimidazole is disclosed in the aforesaid U.S. Pat. No. 3,509,108. As disclosed therein aromatic polybenzimidazoles may be prepared by initially reacting the monomer in a melt phase polymerization at a temperature above about 200°C. and a pressure above 50 psi (e.g., 300 to 600 psi) and then heating the resulting reaction product in a solid state polymerization at a temperature above about 300°C. (e.g. 350° to 500°C.) to yield the final product.

The term polybenzimidazole "fibrous material" as used herein includes monofilaments, as well as multifilament fibrous materials, such as yarn, strand, cable, tow, or other continuous or discontinuous fibrous assemblage. In a preferred embodiment of the process the polybenzimidazole fibrous material is a multifilament yarn or a multifilament tow.

As is known in the art, polybenzimidazoles are generally formed into continuous lengths of fibrous materials by solution spinning, that is, by dry or wet spinning a solution of the polymer in an appropriate solvent such as N,N-dimethylacetamide, N,N-dimethylformamide, dimethylsulfoxide or sulfuric acid (used only in wet spinning) through an opening of predetermined shape into an evaporative atmosphere for the solvent in which most of the solvent is evaporated (dry) or into a coagulation bath (wet), resulting in the polymer having the desired filamentary shape.

The polymer solutions may be prepared in accordance with known procedures. For example, sufficient polybenzimidazole may be dissolved in the solvent to yield a final solution suitable for extrusion containing from about 10 to 45 percent by weight of the polymer, based on the total weight of the solution, preferably from about 20 to 30 percent by weight.

One suitable means for dissolving the polymer in the solvent is by mixing the materials at a temperature above the atmospheric boiling point of the solvent, for example 25° to 120°C. above such boiling point and at a pressure of 2 to 15 atmospheres for a period of 1 to 5 hours.

Preferably, the polymer solutions, after suitable filtration to remove any undissolved portions, are dry spun. For example, the solutions may be extruded through a spinneret into a conventional type downdraft spinning column containing a circulating inert gas such as nitrogen, noble gasses, combustion gasses, or superheated steam. Conveniently, the spinneret face is at a temperature of from about 100° to 170°C., the top of the column from about 120° to 220°C., the middle of the column from about 140° to 250°C., and the bottom of the column from about 160° to 320°C. After leaving the spinning column, the continuous filamentary materials are taken up, for example, at a speed within the range of about 50 to 350 meters or more per minute. If the continuous filamentary materials are to be washed while wound on bobbins, the resulting "as-spun" materials may be subjected to a slight steam drawing treatment at a draw ratio of from about 1.05:1 to 1.5:1 in order to prevent the fibers from relaxing and falling off the bobbin during the subsequent washing step. Further details with respect to a method for dry-spinning a continuous length of a polybenzimidazole fibrous material are shown in U.S. Pat. No. 3,502,756 to Bohrer et al. which is assigned to the same assignee as the present invention and is herein incorporated by reference.

The continuous length of polybenzimidazole fibrous material is next washed so as to remove at least the major portion of residual spinning solvent, e.g., so that the washed materials contain less than about 1 percent by weight solvent based on the weight of the continuous filamentary material, and preferably so as to obtain an essentially spinning solvent-free fibrous material (i.e., a fibrous material containing less than about 0.1 percent solvent by weight). Typically, a simple water wash is employed; however, if desired, other wash materials such as acetone, methanol, methylethyl ketone and similar solvent-miscible and volatile organic solvents may be used in place of or in combination with the water. The washing operation may be conducted by collecting the polybenzimidazole fibrous material on perforated rolls or bobbins, immersing the rolls in the liquid wash bath and pressure washing the fibrous material, for example, for about 2 to 48 hours or more. Alternatively, the continuous length of polybenzimidazole fibrous material may be washed on a continuous basis by passing the fibrous material in the direction of its length through one or more liquid wash baths (e.g., for 1 to 10 minutes). Any wash technique known to those skilled in the art may be selected.

The continuous length of polybenzimidazole fibrous material may next be dried to remove the liquid wash bath by any convenient technique. For instance, the drying operation for bobbins of yarn may be conducted

at a temperature of about 150° to 300°C. for about 2 to 100 hours or more. Alternatively, the continuous length of polybenzimidazole fibrous material may be dried on a continuous basis by passing the fibrous material in the direction of its length through an appropriate drying zone (e.g., an oven provided at 300° to 400°C. for 1 to 2 minutes). If drying is employed, preferably the drying temperature does not exceed about 250°C. for several hours or 400°C. for more than 1 minute, as above these limits degradation of the fiber may occur.

The polybenzimidazole fibrous material preferably next is hot drawn at a draw ratio of about 2:1 to 5:1 in order to enhance its orientation. Representative draw procedures are disclosed in commonly assigned U.S. Pat. No. 3,622,660, and Ser. No. 297,511, filed Oct. 13, 1972 which issued as U.S. Pat. No. 3,849,529.

The Formation of a Polybenzimidazonium Salt

The large denier polybenzimidazole fibrous material is contacted with a solution of an acid having a pK_A below about 4.5 (preferably below about 3.5) while at an elevated temperature to transform the polybenzimidazole to a polybenzimidazonium salt wherein the anion of the salt is derived from the acid.

The acid selected may be organic or inorganic in nature and preferably is relatively non-volatile and incapable of decomposition at the treatment temperature selected. The pK_A value of a given acid conveniently may be ascertained by determining the negative logarithm of the K_A for acid in a 0.1M aqueous solution at 25°C. Those acids having a pK_A value much above about 4.5 possess insufficient strength to be useful in the production of the desired salt. Suitable acids include the mineral acids, monobasic acid and dibasic carboxylic acids, and sulfonic acids.

Representative inorganic acids include: sulfamic acid, sulfuric acid, hydrochloric acid, phosphoric acid, perchloric acid, hydrobromic acid, hydrofluoric acid, hydroiodic acid, etc.

Representative carboxylic acids include: acetic acid, oxalic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monofluoroacetic acid, difluoroacetic acid, trifluoroacetic acid, substituted benzoic acids, salicylic acid, etc.

Representative sulfonic acids include: benzene sulfonic acid, 6-toluene sulfonic acid, m-toluene sulfonic acid, p-toluene sulfonic acid, 2,4-xylene sulfonic acid, toluene-2,4-disulfonic acid, 2-naphthalene sulfonic acid, bisphenol disulfonic acid, chlorosulfonic acid, methane sulfonic acid, trifluoromethane sulfonic acid, etc.

The particularly preferred acids for use in the process are sulfamic acid, phosphoric acid, sulfuric acid, hydrochloric acid and acetic acid.

The solvent utilized to form the solution of the acid preferably is aqueous in nature; however, other solvents such as N-propanol, ethyleneglycolmonomethyl ether, methylene chloride, methanol, etc., may alternatively be employed.

The acid preferably may be provided in the solvent in a concentration of about 1 to 10 percent by weight

based upon the total weight of the solution, and most preferably in a concentration of about 2 to 5 percent by weight. The acid solution preferably is provided in a quantity such that its weight exceeds that of the polybenzimidazole fibrous material undergoing treatment by about 10 to 40 times. Also the acid preferably is provided in a quantity such that at least 1 equivalent of acid (e.g. 1 to 2 equivalents of acid) reacts with each repeat unit of the polymer to form the polybenzimidazonium salt. An aqueous solution of the acid optionally may include a swelling agent for the polybenzimidazole dissolved or dispersed therein in order to aid in the uniform production of the polybenzimidazonium salt throughout the fibrous material. Representative swelling agents include: benzyl alcohol, 2-phenoxyethanol, or other partially soluble solvents having a solubility parameter in water between 11 and 13. The swelling agent preferably is provided in a concentration of about 3 to 20 percent by weight based upon the total weight of the solution, and most preferably in a concentration of about 5 to 10 percent by weight. The particularly preferred swelling agent for use in the process is benzyl alcohol.

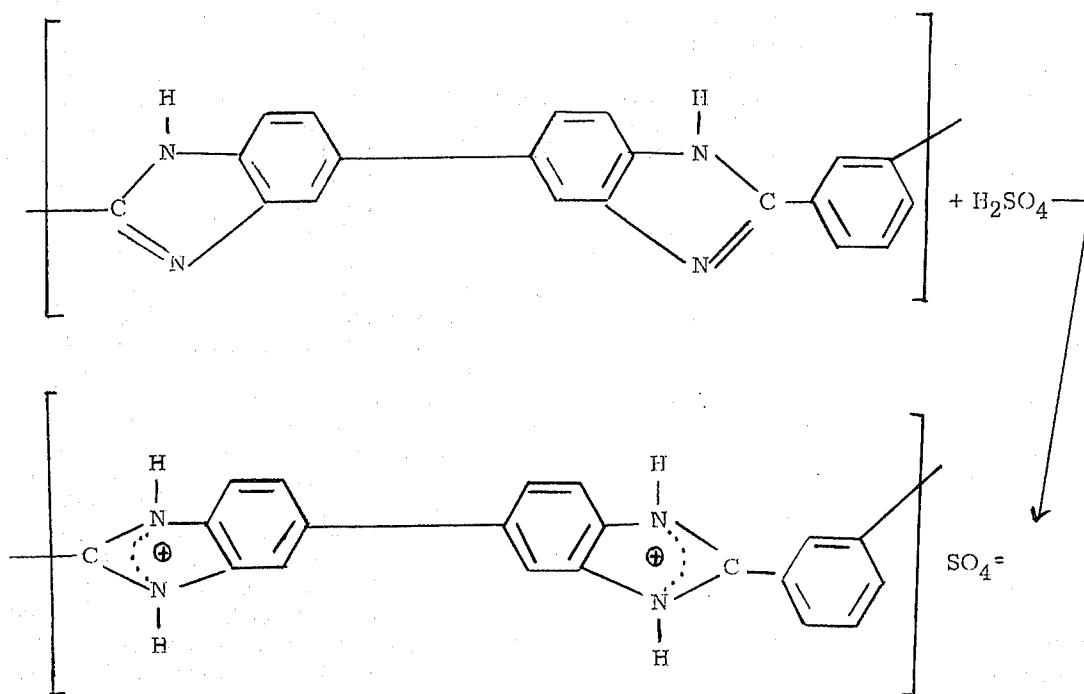
The solution of the acid preferably is provided at a temperature of about 50° to 100°C. (e.g. about 90° to 98°C.) when contacted with the polybenzimidazole fibrous material. It is recommended that the fibrous material be immersed in the solution of the acid in such a manner that direct contact with the solution throughout the fibrous material is maximized. For instance, a continuous length of the fibrous material while wound upon a frame or support to a limited thickness may be positioned in the solution. Alternatively, a continuous length of the fibrous material may be continuously passed through the solution in the direction of its length while substantially suspended therein. Suitable residence times for the formation of the polybenzimidazonium salt commonly range from about 2 to 50 minutes (e.g. 20 to 40 minutes) while in contact with the solution of acid. Longer residence times may be selected without commensurate advantage.

Alternatively, the polybenzimidazonium salt may be formed by contact of the swollen as-spun polybenzimidazole fibrous material with the solution of acid as described.

After the acid treatment the fibrous material preferably is washed, (i.e. rinsed) with water to remove excess acid, and is dried (e.g. at 100 to 200°C. for 15 minutes in a circulating air oven).

The formation of the polybenzimidazonium salt surprisingly has been found to render the fibrous material capable of undergoing stabilization in an oxidizing atmosphere on a more expeditious basis thereby effectively overcoming stabilization difficulties commonly associated with large denier polybenzimidazole fibrous materials.

The formation of a polybenzimidazonium sulfate salt upon reaction of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole with sulfuric acid is illustrative of the salt formation reaction and can be represented by the following equation:



As indicated previously, it is not essential that 2 equivalents of acid react with each repeat unit of the polymer to form the polybenzimidazonium salt.

Once the salt formation reaction is complete the fibrous material continues to exhibit its original fibrous configuration, but exhibits substantially different properties. For instance, the tendency for the fibrous material to shrink in length when heated in an unrestrained state in an incandescent flame at about 500°C. is commonly reduced from about 80 percent to 4 or 5 percent. Shifts in uv absorption maxima commonly are observed, e.g. when sulfuric acid is used to form the salt a thin polymer film on quartz may exhibit a value of 252,340 nm while the control of untreated poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole film exhibits a value of 258,357 nm. Solubility changes and thermal stability changes may be observed.

Density changes may be observed. For instance when fibers of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole are treated in aqueous solutions of 3 percent acid and 6 percent benzyl alcohol swelling agent for 40 minutes at 95°C. the following densities were recorded for the resulting fibers.

Acid Utilized	Density of Fiber (gm./c.c.)
Sulfuric acid	1.39
Phosphoric acid	1.40
Sulfamic acid	1.38
Hydrochloric acid	1.31
p-toluene sulfonic acid	1.33
Acetic acid	1.29
Trifluoroacetic acid	1.32
Oxalic acid	1.35
Salicylic acid	1.30
Untreated control	1.27
Control subjected to benzyl alcohol and water only	1.29

Also, crystallinity changes may be apparent. Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole fibers generally

exhibit two broad equatorial scattering areas indicating an amorphous somewhat oriented structure. After the acid treatment to form the polybenzimidazonium salt two somewhat sharper arcs appear, one on the equator [A] representing aromatic layer packing, and the other on the meridian [B] indicating order in the fiber direction. The crystallite sizes (in Angstroms) of representative acidified materials in the two directions are as follows:

Acid Utilized	[A]	[B]
Sulfuric acid	16	19
Hydrofluoric acid	16	15
Phosphoric acid	20	18
Perchloric acid	22	32
Sulfamic acid	19	19

The Thermal Stabilization

The fibrous material following the formation of the polybenzimidazonium salt is heated for a relatively brief residence time in a molecular oxygen-containing gaseous atmosphere at a temperature of about 300° to 530°C. to oxidize the fibers and to render the same capable of undergoing carbonization while retaining the original fibrous configuration substantially intact. The preferred oxygen-containing gaseous atmosphere is air; however, other gaseous atmospheres containing a greater or lesser concentration of oxygen produce equally satisfactory results.

The stabilization treatment may be carried out on either a batch or a continuous basis with the large denier fibrous material being either (1) statically positioned within the stabilization zone, or (2) continuously passed through the stabilization zone in the direction of its length. When the process is carried out on a batch basis, a continuous length of the fibrous material may be wound upon a support (e.g. a stainless steel bobbin) and placed in the stabilization zone. The stabilization

treatment is preferably carried out while the fibrous material is maintained at a substantially constant length.

Suitable residence times for the stabilization reaction commonly range from about 1 to 30 minutes. Longer residence times may be utilized without commensurate advantage.

The period of time required to complete the stabilization reaction within the gaseous atmosphere generally is inversely related to the temperature of the gaseous atmosphere, and also is influenced to some degree by the denier of the fibrous material. During the stabilization reaction it may be desirable that the fibrous material be gradually raised to the maximum stabilization temperature if the resulting product is to exhibit optimum physical properties. A representative heating profile which is particularly advantageous when the polybenzimidazonium salt was formed with the aid of sulfuric acid, or sulfamic acid, is as follows: heat at 300°C. for 10 minutes, at 400°C. for 10 minutes, and at 465°C. for 5 minutes. When the polybenzimidazonium salt is formed with the aid of an acid such as phosphoric acid or acetic acid, the entire stabilization reaction may be carried out at a relatively constant temperature of about 465°C. for 5 minutes. The exact stabilization heating conditions for optimum results within the range of about 300° to 530°C. may be determined by simple experimentation.

The stabilized fibrous material formed in accordance with the present process is black in appearance which is usually accompanied by a purple tinge, retains its original fibrous configuration substantially intact, and is capable of undergoing carbonization when heated in an inert gaseous atmosphere (e.g. at a temperature of 1000°C.) without loss of its configuration (e.g. through coalescence or melting). Also, the fiber can be tensioned upon continuous carbonization in the absence of breakage. Additionally the stabilized fibrous material commonly exhibits a bound oxygen content of about 2-8 percent by weight as determined by the Unterzaucher, or other suitable analysis.

The theory whereby the initial conversion of the large denier polybenzimidazole fibrous material to a polybenzimidazonium salt is capable of expediting the subsequent stabilization reaction so that the desired stabilization can be accomplished in minutes rather than hours is considered complex and incapable of simple explanation when compared with the residence times required in the prior art for the same fibers. The results achieved are considered to be surprising and unexpected.

The Formation of a Large Denier Carbon Fiber

The resulting stabilized fibrous material is heated in a non-oxidizing gaseous atmosphere at a temperature of at least 1000°C. until a carbonaceous fibrous material is formed which contains at least 90 percent carbon by weight (preferably at least 95 percent carbon by weight) and retains the original fibrous configuration substantially intact. Carbonization or carbonization and graphitization may be accomplished in accordance with conventional techniques, e.g. the utilization of induction furnaces, resistance heated furnaces, or reducing flames as disclosed in commonly assigned U.S. Pat. No. 3,449,077.

In a preferred embodiment of the process the non-oxidizing gaseous atmosphere is an inert gaseous atmo-

sphere selected from the group consisting of nitrogen, argon and helium. The particularly preferred gaseous atmosphere is nitrogen.

The higher the temperature of the non-oxidizing gaseous atmosphere the greater the degree of graphitic carbon formed within the fiber and the greater the Young's modulus of the fiber. Temperature profiles may be utilized wherein the fiber is heated in a non-oxidizing gaseous atmosphere having a temperature up to about 3000°C. Residence times at a temperature of at least 1000°C. commonly range from about 2 to 20 minutes. Lesser residence times may be utilized if the resulting stabilized fibrous material is heated in a reducing flame.

The carbonization or carbonization and graphitization may be carried out on a batch or continuous basis. Since comparable residence times are required for the stabilization treatment and the carbonization treatment, these steps of the process optionally may be carried out in tandem with a continuous length of fibrous material being passed in the direction of its length through the appropriate heating zones.

Commonly the carbon fibers formed in the present process have a denier per filament of about 30 to 400 (e.g. 70 to 350), and an average diameter of about 0.002 to 0.008 inch. The diameter of the carbon fiber product is largely determined by the diameter of the starting material but is generally less than that of the starting material due to loss of non-carbon atoms during the carbonization treatment and possible stretching during stabilization and carbonization.

The large denier carbon fibers formed in the present process may be incorporated in a matrix material (e.g. a polymeric or metallic matrix) to form a composite article having an enhanced compressive strength to tensile strength ratio. The large denier carbon fibers are particularly suited for incorporation in a metallic matrix, e.g. a matrix of manganese, aluminum, or copper. If desired, a protective coating, such as silicon or chromium, may be applied to the fibers prior to incorporation in a metallic matrix rather than incorporating the fibers directly in the matrix. Also, the large denier carbon fibers may be substituted for a tungsten fiber prior to the application of a coating boron to yield a fiber suitable for incorporation in a composite article having a lesser density than a common boron fiber.

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 polybenzimidazole monofilament, namely poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, is selected as the exemplary polybenzimidazole for use in carrying out the process of this invention. The monofilament has a denier per filament of 400 and a fiber diameter of 0.008 inch. The monofilament is formed in accordance with the procedure described in commonly assigned U.S. Pat. No. 3,526,693 of R. N. Rulison and J. P. Riggs and has been hot drawn at a draw ratio of 2.5:1.

The monofilament was wrapped about a mandrel and immersed for 30 minutes in a solution consisting of 2 percent by weight sulfuric acid, 6 percent by weight benzyl alcohol swelling agent, 0.06 percent by weight of an anionic surfactant (i.e. a sodium salt of a complex phosphate ester sold under the designation GAFAC

MC-470 surfactant), and 91.94 percent by weight water provided at a temperature of 95°C. to form a polybenzimidazonium salt having a sulfate anion. The monofilament is next washed in water to remove excess acid and is dried in air at 200°C. for 15 minutes. The formation of the salt is evidenced by changes in solubility, fiber color, density, uv absorption, crystallinity and the presence of 5.3 percent by weight sulfur therein as determined by x-ray fluorescence. Following the salt formation reaction the monofilament retains its original fibrous configuration intact and exhibits a brighter appearance.

The monofilament while wrapped on a suitable mandrel is thermally stabilized by heating in a circulating air oven in accordance with the following heating schedule: 10 minutes at 300°C., 10 minutes at 400°C. and 5 minutes at 465°C. The stabilized monofilament is black in appearance, and retains its original fibrous configuration intact.

The stabilized monofilament while in a holder is carbonized in a tube furnace containing a circulating nitrogen atmosphere. The monofilament over a period of 3 minutes gradually was inserted in the furnace which was preheated to 1100°C., retained therein for 15 minutes while at 1100°C., and subsequently withdrawn. The resulting large denier carbonaceous fibrous material contains in excess of 90 percent carbon by weight, retains its original fibrous configuration intact, has a mean denier of 280 and a mean fiber diameter of about 0.007 inch, a filament strength of 61,000 psi, a break elongation of 0.42 percent, a tensile modulus of 14.5 million psi, a density of 1.39 gm./c.c., and is suited for use as fibrous reinforcement in a polymeric or metallic matrix material.

EXAMPLE II

Example I is repeated with the exception that sulfamic acid is substituted for sulfuric acid in the polybenzimidazonium salt formation reaction to form a salt having a $\text{H}_2\text{N}-\text{SO}_2\text{O}^-$ anion. Also, the processing conditions are modified as indicated. The thermal stabilization solely is conducted in air for 5 minutes at 465°C. During carbonization the fibrous material is maintained for 3 minutes at 1100°C. The resulting carbon filament has a mean denier of 279, a tensile strength of 60,000 psi, a break elongation of 0.75 percent, a tensile modulus of 8 million psi, and a density of 1.38 gr./c.c.

EXAMPLE III

Example I is repeated with the exception that phosphoric acid is substituted for sulfuric acid in the polybenzimidazonium salt formation reaction to form a salt having a phosphate anion. Also, the processing conditions are modified as indicated. The thermal stabilization solely is conducted in air for 5 minutes at 465°C. During carbonization the fibrous material is maintained for 2 minutes at 1100°C. The resulting carbon filament has a mean denier of 255, a tensile strength of 80,000 psi, a break elongation of 0.41 percent, a tensile modulus of 19 million psi, and a density of 1.40 gm./c.c.

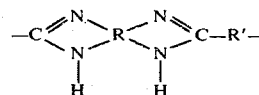
Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art (e.g. the process could be carried out on a continuous basis, etc.). Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. An improved process for the formation of a large denier carbonaceous fibrous material comprising:

- contacting a polybenzimidazole fibrous material having a denier per filament of about 50 to 600 with a solution of an acid having a pK_a value below about 4.5 while at an elevated temperature to transform said polybenzimidazole to a polybenzimidazonium salt wherein the anion of said salt is derived from said acid,
- heating said fibrous material following contact with said acid in an oxygen-containing gaseous atmosphere at a temperature of about 300° to 530°C. to render said fibrous material capable of undergoing carbonization while retaining the original fibrous configuration substantially intact, and
- heating said resulting fibrous material in a non-oxidizing gaseous atmosphere at a temperature of at least 1000°C. until a carbonaceous fibrous material is formed which contains at least 90 percent carbon by weight and retains the original fibrous configuration substantially intact.

2. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said polybenzimidazole fibrous material consists essentially of recurring units of the formula:



wherein R is a tetravalent aromatic nucleus, with the nitrogen atoms forming the benzimidazole rings paired upon adjacent carbon atoms of said aromatic nucleus, and R' is selected from the group consisting of (1) an aromatic ring, (2) an alkylene group having from 4 to 8 carbon atoms, and (3) a heterocyclic ring selected from the group consisting of (a) pyridine, (b) pyrazine, (c) furan, (d) quinoline, (e) thiophene, and (f) pyran.

3. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said polybenzimidazole fibrous material is poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.

4. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said polybenzimidazole fibrous material has denier per filament of about 100 to 500.

5. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said acid is selected from the group consisting essentially of sulfamic acid, phosphoric acid, sulfuric acid, hydrochloric acid, and acetic acid.

6. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said solution of said acid utilized in step (a) is provided at a temperature of about 50° to 100°C. when contacted with said fibrous material.

7. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 6 wherein said contact is conducted for about 2 to 50 minutes.

8. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said oxygen-containing gaseous atmosphere is air.

9. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said fibrous material following contact with said acid is heated in said oxygen-containing atmosphere of step (b) for about 1 to 30 minutes.

10. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said non-oxidizing gaseous atmosphere of step (c) is selected from the group consisting essentially of nitrogen, argon, and helium.

11. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 1 wherein said resulting fibrous material is heated in said non-oxidizing gaseous atmosphere of step (c) for about 2 to 20 minutes.

12. An improved process for the formation of a large denier carbonaceous fibrous material comprising:

- a. contacting a poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole fibrous material having a denier per filament of about 100 to 500 with an aqueous solution of an acid selected from the group consisting essentially of sulfamic acid, phosphoric acid, sulfuric acid, hydrochloric acid and acetic acid, while at a temperature of about 50° to 100°C. for a residence time of about 2 to 50 minutes to transform said poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole to a polybenzimidazonium salt wherein the anion of said salt is derived from said acid,
- b. heating said resulting fibrous material following contact with said acid in an oxygen-containing gaseous atmosphere at a temperature of about 300° to 530°C. for a residence time of about 1 to 30 minutes to render said fibrous material capable of un-

dergoing carbonization while retaining the original fibrous configuration substantially intact, and

- c. heating said resulting fibrous material at a temperature of at least 1000°C. in a non-oxidizing gaseous atmosphere selected from the group consisting essentially of nitrogen, argon, and helium for a residence time of about 2 to 20 minutes until a carbonaceous fibrous material is formed which contains at least 90 percent carbon by weight and retains the original fibrous configuration substantially intact.

13. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 12 wherein said fibrous material is a continuous length of a multifilament yarn.

14. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 12 wherein said fibrous material is a continuous length of a multifilament tow.

15. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 12 wherein said aqueous solution of said acid additionally includes a swelling agent for said fibrous material.

16. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 15 wherein said swelling agent is benzyl alcohol.

17. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 15 wherein said oxygen-containing gaseous atmosphere of step (b) is air.

18. An improved process for the formation of a large denier carbonaceous fibrous material in accordance with claim 15 wherein said non-oxidizing gaseous atmosphere of step (c) is nitrogen.

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