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(54) **ELECTROPHORETIC PROCESS FOR THE DEPOSITION OF MULTIPLE COATINGS ON FIBERS**

**ELEKTROPHORETISCHES VERFAHREN ZUM AUFBRINGEN MEHRFACHER
BESCHICHTUNGEN AUF FASERN**

**PROCEDE D'ELECTROPHORESE POUR DEPOSITION DE REVTEMENTS MULTIPLES SUR DES
FIBRES**

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Description

Technical Field

The present invention relates to the area of metallic oxide coated fibers, and particularly to the application of multiple layers of oxide or mixed oxide coatings to a filament, wire, or tow by electrophoretic deposition of colloidal materials from sols to encase a conductive fiber core. More particularly, it relates to the use of sols of oxide materials, such as the oxides of aluminum, zirconium, titanium, chromium, lanthanum, hafnium, yttrium, and mixtures thereof, such as yttria-aluminagarnet (YAG), and their multiple depositions on substrates by electrophoresis, to provide even, dense, and uniformly coated fibers, while avoiding the costly preparatory steps of prior art techniques for deposition of a ceramic material on a substrate. In addition, the invention encompasses deposition of metallic oxide coatings upon a fiber substrate also bearing an electrophoretically deposited layer of a material such as carbon, silicon, boron, or boron nitride.

Background Art

It is well known to apply coatings to the surface of a body so as to obtain surface properties which differ from those of the body. This may be done to achieve a variety of improvements, such as increased toughness, high temperature capability, oxidation resistance, wear resistance, and corrosion resistance. By providing surface coatings of the appropriate characteristics, it is possible to substantially lower the cost of an article built to specific property requirements. For example, ceramics have frequently been utilized to provide a surface coating over a less temperature resistant metallic article, to permit use of that article in higher temperature environments. The application of such a coating is well recognized as a less expensive means for achieving a high temperature capability than producing the entire element or article from a more costly material capable of withstanding the elevated temperature. In addition to such application to planar substrates, articles, and surfaces, there is likewise a need for means to apply adherent, dense, and controllable oxide coatings to fibers for various purposes, such as for use in metal matrix composites to reduce thermal expansion mismatch between a reinforcing fiber and a metal matrix, as debonding layers, to provide oxidation protection to a fiber, and to provide barrier or surface modification coatings to fibers. There is a specific need for method for application of a plurality of such coatings to a single fiber substrate at a high rate of speed.

In the past, various processes have been used to deposit ceramic materials upon a substrate. These include the application of glazes, enamels, and coatings; hot-pressing materials at elevated pressure and temperature; and vapor deposition processes such as evap-

oration, cathodic sputtering, chemical vapor deposition, flame spraying, and plasma spraying. In addition, electrophoresis has been attempted, as have other specialized techniques, with limited success in application.

For example, the enamelling industry has used the electrodeposition of ceramic materials for some time. In the application of a ceramic coating by this technique, a ceramic material is milled or ground to a small particulate or powder size, placed in suspension, and electrophoretically deposited on the substrate. A similar method is the deposition of a ceramic coating from a slurry made up of a powder in suspension, usually in an aqueous medium. A major problem with these techniques is that powder particle sizes below about 2 μm were difficult to obtain, thus limiting the quality of coatings produced, as well as the possibility of application to a wire or fibrous substrate.

Sol-gel technology has recently evolved as a source of very fine sub-micron ceramic particles of great uniformity. Such sol-gel technology comprises essentially the preparation of ceramics or metallic oxides by low temperature hydrolysis and peptization of metal oxide precursors in solution, rather than by the sintering of compressed powders at high temperatures.

In the prior art, much attention has been given to the preparation of sols of metallic oxides (normally actually metal hydroxides or metal hydrates) by hydrolysis and peptization of the corresponding metal alkoxide, such as aluminum sec-butoxide $[\text{Al}(\text{OC}_4\text{H}_9)_3]$, in water, with an acid peptizer such as hydrochloric acid, acetic acid, nitric acid, and the like. The hydrolysis of aluminum alkoxides is discussed in an article entitled "Alumina Sol Preparation from Alkoxides" by Yoldas, in American Ceramic Society Bulletin Vol. 54, No. 3 (1975), pages 289-290. This article teaches the hydrolysis of aluminum alkoxide precursor with a mole ratio of water to precursor of 100:1, followed by peptization at 90° F (32.2°C) with 0.07 moles of acid per mole of precursor. After gelling and drying, the dried gel is calcined to form alumina powder.

In U.S. Patent 4,532,072, of Segal, an alumina sol is prepared by mixing cold water and aluminum alkoxide in stoichiometric ratio, allowing them to react to form a peptizable aluminum hydrate, and peptizing the hydrate with a peptizing agent in an aqueous medium to produce a sol of an aluminum compound.

In Clark et al, U.S. Patent 4,801,399, a method for obtaining a metal oxide sol is taught whereby a metal alkoxide is hydrolysed in the presence of an excess of aqueous medium, and peptized in the presence of a metal salt, such as a nitrate, so as to obtain a particle size in the sol between 0.0001 μm and 10 μm .

In Clark et al, U.S. Patent 4,921,731, a method is taught for ceramic coating a substrate, such as a wire, by thermophoresis of sols of the type prepared by the method of U.S. Patent 4,801,399. In addition, Clark et al, in abandoned U.S. Patent Application 06/841,089, filed February 25, 1986, teach formation of ceramic

coatings on a substrate, including filaments, ribbons, and wires, by electrophoresis of such sols. However, the examples of this application indicate that the coatings obtained using electrophoresis were uneven, cracked, and contained voids or bubbles, and often peeled, flaked off, and/or pulled apart. Throughout, the evolution of hydrogen bubbles at the cathode during electrophoresis was noted.

Additional teachings of the electrophoretic deposition of various oxides are numerous. Such references include U.S. Patent 2,956,937 of Thomson; U.S. Patent 3,575,838 of Hughes; U.S. Patent 3,896,018 of Powers et al; U.S. Patent 4,810,339 of Heavens et al; and U.S. Patent 4,975,417 of Koura.

It is thus seen that a need exists for a method for the electrophoretic deposition of oxide coatings on filaments, fiber tows, or wire substrates, particularly so as to form fibers bearing a multiplicity of layers of differing oxide materials. There is a particular need for a method for the preparation of oxide coated fibers suitable for use as reinforcing elements in metal matrix composites.

SUMMARY OF THE INVENTION

In the pursuit of a method for the preparation of defect-free metallic oxide coated fibers, applicants have developed a novel electrophoretic deposition process especially suitable for the deposition of multiple layers of coating material, and especially metallic oxides, upon a fiber.

As used herein, the term "filament" shall refer to a single strand of fibrous material, "fiber tow" shall refer to a multi-filament yarn or array of filaments, a "wire" shall refer in general to metallic filaments or tows, a "fiber core" shall indicate a filament, fiber tow, or wire suitable for coating by the process of this invention, and the term "metallic oxide coated fiber" or "coated fiber" shall refer to a fiber core of an electrically conductive material, or a material which has been made to be conductive such as by a flash coat of carbon or a metallizing layer, upon which has been deposited multiple layers of metallic oxides selected from the group consisting of alumina, zirconia, titania, chromia, lanthanum oxide, hafnia, yttria, or mixtures thereof, such that the diameter of the fiber core is greater than the thickness of the applied coating of metallic oxide or oxides. Conversely, for convenience, the terms "metallic oxide fiber" or "fiber" shall be used to refer to an electrically conductive fiber core material upon which has been deposited multiple metallic oxide layers, such that the thickness of the applied layers exceeds the diameter of the fiber core. This distinction of relative thickness of surface layer and core is normally recognized in industry to define between coated fiber and fiber. In either case, of course, the fiber core material may, if desired, be removed by such techniques as acid dissolution, combustion, etc., to leave a hollow cylinder of concentric layers of metallic oxide or oxides, which may, of course, then be referred to as a metallic

oxide fiber.

Further, for convenience and consistency, the term "oxide" shall be used in reference to the particulate material present in the metallic oxide sols employed in the present invention, which material may actually be in the form of an hydroxide or hydrate, rather than an oxide per se. Thus, while the hydrolysis and peptization of aluminum sec-butoxide may actually result in the formation of a sol comprising aluminum hydroxide, for purposes of the present disclosure, this sol shall be referred to herein as an aluminum oxide sol, or an alumina sol.

As used herein, the term sol shall refer not only to sols of metaloxides, prepared by such methods as by the hydrolysis and peptization of the corresponding metal alkoxide, but more generally to a dispersion of discrete particles (such as a powder) which are small enough to remain suspended in an appropriate viscosity medium, such as water and/or alcohol.

It is an object of this invention to provide a method for the electrophoresis of multiple sols so as to provide a fiber bearing a number of concentric coatings of metallic oxide. It is another object of this invention to provide a method which may be utilized to obtain a metallic oxide coated fiber comprising an intermediate layer or layers of such materials as carbon, silicon, boron, or boron nitride. It is a still further object of this invention to provide a method which may be utilized to obtain a highly uniform, defect-free metallic oxide coated fiber comprising a plurality of metallic oxide layers.

The present invention accomplishes these and other goals by providing a method for the deposition of multiple coating layers upon a fiber substrate, said method comprising the steps of:

- a) providing a plurality of sols comprising particulate coating material selected from the group consisting of carbon, silicon, boron, boron nitride, alumina, zirconia, titania, chromium oxide, lanthanum oxide, hafnia, yttria, and mixtures thereof;
- b) electrophoretically depositing a particulate coating material from one such sol onto an electrically conductive fiber core by applying a direct current potential between said fiber core and an oppositely charged electrode for sufficient time to obtain a uniform coating thereof on said fiber core;
- c) removing the coated fiber core from said sol;
- d) repeating steps b and c with successive sols selected from said plurality of sols until the desired number of layers of particulate coating material have been applied;
- e) heating the fiber core and particulate coating materials deposited thereupon after said fiber core emerges from the final such sol, so as to remove water and alcohol from said layers;
- f) heating the multiply coated fiber at a temperature sufficient to cure the various layers; and
- g) recovering the coated fiber.

More particularly, the present invention relates to a method for preparing multiple layer coatings on a fiber substrate, by:

- a) providing a plurality of sols comprising particles selected from the group consisting of alumina, zirconia, titania, chromium oxide, lanthanum oxide, hafnia, yttria, and mixtures thereof, said particles being less than 150 Angstroms (15nm) in size, each said sol also comprising an alcohol such that the molar ratio of said alcohol to said metal hydrate is from about 50 to about 70;
- b) electrophoretically depositing particles from one such sol onto an electrically conductive fiber core by applying a direct current potential between said fiber core and an oppositely charged electrode, said potential being from about 0.1 to about 100 volts, while providing means for removal of hydrogen gas generated by said electrophoresis;
- c) removing the thus coated fiber core from said sol;
- d) repeating steps b and c with successive sols of the same or differing metal oxides until the desired thickness of metallic oxide layers has been applied;
- e) heating the fiber core and metal oxide particles deposited thereupon after said fiber core emerges from the final such sol, so as to form a green coating of said metal oxides on said fiber;
- f) heating the multiply coated fiber at a temperature sufficient to cure the various metallic oxide layers; and
- g) recovering the metallic oxide coated fiber.

The present invention further provides a method for the continuous production of a metal oxide fiber, comprising:

- a) continuously passing an electrically conductive fiber core through an electrophoresis cell containing a sol prepared by the steps of
 - (1) concurrent hydrolysis and alcoholization of an organometallic compound in an aqueous medium comprising water and an alcohol;
 - (2) peptization of this reaction mixture with a monovalent acid or acid source;
 - (3) dehydration and de-alcoholization of the reaction mixture by removal of the excess aqueous phase;
 - (4) dewatering and further removal of unreacted alcohol by evaporation; and
 - (5) re-alcoholization by addition of a second alcohol to the concentrated sol to form a sol wherein the molar ratio of alcohol to metal oxide is from about 50 to about 70, and the particle size of said metal oxide is from about 10 to about 150 Angstroms (about 1 to about 15 nm);
- b) applying a potential between said fiber core and

another electrode immersed in said sol, whereby metal oxide particles are continuously deposited on said fiber core;

- c) decreasing the evolution of hydrogen by operating said electrophoresis cell at a potential of from about 1 to about 50 volts, while providing means for the dispersal and removal of hydrogen gas from the electrophoresis cell;
- d) repeating the above steps a, b, and c with successive sols of the same or differing metal oxides until the desired number of layers of metallic oxide have been applied;
- d) heating the fiber core and metal oxide particles deposited thereupon after said fiber core emerges from the final such sol, so as to form a green coating of said metal oxides on said fiber;
- f) heating the multiply coated fiber at a temperature sufficient to cure the various metallic oxide layers;
- g) recovering the metallic oxide coated fiber; and
- h) removing the fiber core to recover a hollow metallic fiber.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents a schematic of apparatus suitable for use in the present invention for the application of a plurality of coatings to a fiber core by electrophoresis.

Figure 2 represents a possible apparatus suitable for deposition of a plurality of coatings to a fiber core, in which polarities are changed in successive coating applications.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is suitable for use in producing metallic oxide fibers comprising a plurality of concentric metallic oxide layers. In addition, the method disclosed herein may be used to produce multiple layers of varying compositions on a fiber, and to thus obtain composite fibers comprising metallic oxides.

The sols utilized in the method of the present invention may be produced from a variety of organometallic compounds, to yield metal oxides such as alumina, zirconia, titania, chromium oxide, lanthanum oxide, hafnia, yttria, and mixtures thereof, such as yttria-alumina-garnet, $3Y_2O_3 \cdot 5Al_2O_3$, hereinafter referred to as YAG. While the present disclosure is directed to the use of these specifically enumerated metallic oxides, and particularly to those metallic oxides deposited from the sols specifically enumerated herein, the invention is not to be limited thereto, and should be considered to be applicable to any metallic oxides which may be electrophoretically deposited from sols in accordance with the teachings of this invention, or to any materials such as carbon, silicon, boron, and boron nitride, which are available as discrete particles of small enough size to remain suspended in an appropriate medium such as

water and/or alcohol, and having viscosity such that electrophoresis is possible.

Electrophoresis is an electrodeposition technique whereby minute particles of a normally nonconductive material in colloidal suspension are subjected to an external electric field and thereby caused to migrate toward a specific electrode. Colloids in solution are known to develop a surface charge relative to the suspension medium, as a result of any of a number of possible mechanisms, such as lattice imperfection, ionization, ion absorption, and ion dissolution. In the case of metallic oxides such as alumina, the surface charge is the result of ionization, and is generally positive in the preferred pH range, below about 7. For a sol to be electrophoretically deposited, the particulate matter thereof must possess a surface charge sufficient to overcome the coefficient of drag present in the sol subjected to the electric field.

During electrophoresis, positively charged colloids normally migrate toward a cathodic electrode, forming a compact layer of particles thereupon. The physical properties of the deposited coatings are related to their compaction on, and adherence to, the substrate. Generally, the greater the compaction of the colloidal particles deposited upon the substrate, the better the mechanical properties of the coating and the greater the protection afforded thereby. Conversely, the higher the concentration of water present in the sol, the less efficient the deposition process, and the more porous the coating deposited. For this reason, and others enumerated hereinafter, it has been found advantageous to limit the amount of water in the sol, such as by dewatering and adding alcohol to the sol, when a dense coating is desired. Of course, when a porous layer or layers are desired, such as for thermal insulation, the presence of a higher concentration of water may be advantageous.

The present invention may be utilized to electrophoretically deposit a plurality of coatings on a wide range of fiber cores, both metallic and non-metallic. Any fiber core may be coated in accordance with this invention, if it is electrically conductive, or can be so treated as to be made electrically conductive. For example, fibers of aluminum, carbon, copper, silver, platinum, etc., are normally conductive, while fibers of cotton, polyester, etc., may be made conductive to be coated in accordance with the present invention. Such fibers may, for example, be coated with a conductive metal or carbon, by conventional coating techniques such as chemical vapor deposition, physical vapor deposition, etc., dependent upon the specific materials. Exemplary fiber core materials include non-metallic materials such as carbon, glass, silicon carbide, silicon nitride, alumina, sapphire, organic fiber materials such as cotton, polyester, and wool, and such metals as aluminum, iron, chromium, nickel, tantalum, titanium, molybdenum, boron, tungsten, rhenium, niobium, and alloys thereof. The diameter of the fiber core is not critical, and may be chosen in accordance with the desired diameter and end

usage of the fiber to be produced. Core diameters of from about 0.1 mil (2.5 μm) to about 3 mil (76 μm) are most suitable, recognizing that the present invention may be employed to achieve a coating layer which is thicker than the fiber core, followed by the elimination of said core, so as to form a metallic oxide fiber per se. The final diameter of the coated fiber produced may be from about 0.3 mil (7.6 μm) (or smaller) to about 10 mil (250 μm) (or larger) depending upon the strength and other characteristics required. Fibers considered most suitable for coating in accordance with the present invention include silicon carbide, carbon, boron, and tungsten.

In accordance with the present invention, the preferred sols of metallic oxides have a colloidal particle size of from about 10 Angstroms (1 nm) to about 150 Angstroms (15 nm). A preferred range of particle size is from about 50 Angstroms (5 nm) to about 100 Angstroms (10 nm). Within these ranges of particle sizes, especially good contact of the coating materials is attained with the fiber core, giving excellent adhesion, and excellent packing of the coating particles within the coating layer is obtained, resulting in superior coating properties such as wear resistance, and thermal high temperature capability.

Sols suitable for use in the present invention may be prepared by the hydrolysis and peptization of the corresponding organometallic compounds in an aqueous medium. Preferred organometallic compounds are metal alkoxides, and particularly the metal sec-butoxides, ethoxides, and methoxides of aluminum, and boron for example. Yttrium oxide, and chromium oxide sols may be prepared from the corresponding nitrates. In general, suitable techniques for the preparation of sols for the electrophoretic deposition technique of the present invention are known in the prior art, and may be used in the process of the present invention.

Sols which may be electrophoretically deposited in accordance with the present invention include sols and colloids of metallic oxides, such as the oxides of aluminum, zirconium, titanium, chromium, lanthanum, hafnium, yttrium, and mixtures thereof such as YAG, yttrium aluminum garnet, as well as sols of such materials as carbon, silicon, boron, and boron nitride. While the method of preparation of such sols is not considered a part of the present invention, those sols having the smallest average particulate size are considered most advantageous for use in electrophoresis. In general, sols suitable for use in the present invention may be prepared by the hydrolysis and peptization of a variety of corresponding organometallic compounds in an aqueous medium. Preferred organometallic compounds are metal alkoxides, and particularly the metal sec-butoxides, ethoxides, iso-propoxides, and methoxides of such metals as aluminum. In a preferred method for preparation of a sol suitable for deposition upon a fiber core by the method of the present invention, organometallic compounds are hydrolyzed and peptized to obtain a sol having a colloidal particle size of from about 10

Angstroms (1 nm) to about 150 Angstroms (15 nm). A preferred range of particle size is from about 50 Angstroms (5 nm) to about 100 Angstroms (10 nm). Within these ranges of particle sizes, good contact of the coating materials is attained with the fiber core, giving excellent adhesion, and excellent packing of the coating particles within the coating layer is obtained, resulting in superior coating properties such as wear resistance, and thermal high temperature capability. Suitable techniques for the preparation of such a sol are set forth in co-pending U.S. Patent Application 07/637,717, filed January 1, 1991 by Wright and Dalzell, incorporated herein by reference. This reference teaches the preparation of sols by a process consisting of the steps of concurrent hydrolysis and alcoholization of an organometallic compound in an aqueous medium comprising water and an alcohol; the peptization of this reaction mixture with a monovalent acid or acid source; dehydration and de-alcoholization of the reaction mixture by removal of the excess aqueous phase; dewatering and further removal of unreacted alcohol by evaporation; and re-alcoholization by addition of a second alcohol to the concentrated sol to form a sol wherein the molar ratio of alcohol to metal hydrate is from about 50 to about 70 and the particle size of said metal hydrate is from about 10 to about 150 Angstroms (about 1 to about 15 nm). Other sols may also, however, be used in the process of the present invention, which is not to be limited to any specific sol or process for preparation thereof, subject to the presence of sufficient charge density and the determination of any specific modifications necessary.

A sol suitable for use in the present invention may be prepared in the following manner, in accordance with the teachings of the above cited U.S. Patent Application 07/637,717. While this example is specific to the preparation of an alumina forming sol formulated from an aluminum sec-butoxide precursor, the present invention is not to be limited thereto.

Exemplary Method for Preparation of an Alumina Sol

For the preparation of an alumina sol, a 4000 ml glass reaction vessel was assembled with a variable temperature heating mantel, glass/TEFLON stirring rod with a laboratory mixer having variable speed control, an injection port with a TEFLON tube for insertion of liquids to the bottom of the reaction vessel, and a water-cooled PYREX condenser. After turning on the flow of cooling water to the condenser, 2500 grams (corresponding to 138.8 moles or 2500 ml) of deionized water was metered into the closed reaction vessel, after which the heating mantel was turned on to raise the temperature of the water to between 88°C and 93°C, which temperature was thereafter maintained. The mixer motor was turned on when the water had reached this temperature, and the water was vigorously stirred. In a separately sealable glass transfer container, 357.5 grams

(corresponding to 1.5 moles or 357.5 ml) of aluminum sec-butoxide $[\text{Al}(\text{OC}_4\text{H}_9)_3]$ was mixed with 288.86 grams (corresponding to 3.897 moles or 357.5 ml) of 2-butanol. Experience has taught that exposure of this mixture, or the aluminum sec-butoxide, to air for any longer than the absolute minimum necessary adversely affected the sol produced, so great care was exercised to avoid exposure. The mixture of sec-butoxide and butanol, in the transfer container, was connected to the reaction vessel entry port after the water had reached the desired temperature, and very slowly, over a 5 minute period, metered directly down into the hot deionized water. When all of the mixture had been introduced into the water, the entry port was valved shut and the transfer container removed. The mixture of water, sec-butoxide, and butanol was then permitted to hydrolyse for a period of 1 hour at temperature while stirring vigorously.

After 1 hour, and with the mixture still at temperature and being stirred vigorously, the sol mixture was peptized by connecting a glass syringe containing 8.18 grams (0.224 moles or 6.875 ml) of hydrochloric acid to the vessel entry port. The entry valve was opened and the acid metered directly down into the sol mixture. The valve was then closed, and the syringe removed and refilled with air. The syringe was then reconnected to the entry port, and the air injected into the vessel to ensure that all of the acid had been introduced into the system. The valve was then closed, and the syringe removed.

The heat and stirring were maintained until the sol cleared, about 16 hours. The heat was then turned off and the stirrer and motor assembly removed. After the mixture cooled, the sol and alcohol separated, and the alcohol was removed by pipette. It was found that leaving a small amount of alcohol in the sol did not adversely affect the sol. The pH of the sol was measured and found to be pH 3.90. This initial sol was found to have a good shelf life, and could be stored prior to further processing to obtain a sol suitable for electrophoresis.

A sol was then specifically formulated for the express purpose of making coated fibers in a continuous process. This specific formulation was derived from the initial sol prepared above. A 390 ml sample of the sol prepared above was heated in an open glass beaker to a temperature of approximately 93°C, and the volatiles, alcohol and excess water, evaporated off. The sol was heated until it had been reduced to 250 ml, i.e. to 64 percent of its initial volume, with a noted increase in viscosity. The reduced sol was then removed from the heat and permitted to cool to room temperature. The reduced sol was then re-alcoholized with 750 ml of ethyl alcohol (63 moles of alcohol/mole of aluminum hydrate present). The sol and alcohol were vigorously mixed, then sealed in an air tight container for storage. The pH of this sol was about 3.8. This sol was set aside for 5 months, demonstrating good shelf life, and then subjected to electrophoretic deposition.

To electrophoretically deposit a plurality of coatings on a filament, fiber tow, or wire, hereinafter fiber core,

apparatus such as shown generally in Figure 1 may be used. As previously stated, any fiber core may be coated in accord with this invention, if it is electrically conductive, or can be so treated as to be made electrically conductive. A fiber core may be electrophoretically coated by applying a controlled electrical potential within a colloidal solution of charged particles, with the colloids being driven towards the fiber, at a specific rate controlled by the sol chemistry and the applied electrical potential between the electrodes. The fiber core, being electrically conductive, is the cathodic surface for purposes of electrophoresis of a positively charged sol. If a basic peptizer is utilized in preparation of the sol, the electrodes would, of course, be reversed. Assuming the fiber core is cathodic, the metal anode may be copper, aluminum, silver, gold, platinum, or another electrically conductive metal, but platinum is the material of choice for the anode. Noble metal anodes are preferred, since they will not dissolve and contaminate the coating, but it must be noted that other, less noble consumable metals, such as tin, iron, and yttrium, may be used if it is desired to implant ions or to dope the coating with the metal of the anode. It is to be noted that this means for doping the coating composition is advantageous, since the addition of dilute solutions of dopant material to a sol will frequently destroy the balance and stability of the sol. The colloidal particles collect in a uniform manner about and along the fiber core, producing a thick, dense, uniform, adherent coating, the chemistry and mechanical properties of which are determined by the sol chemistry, applied electrical potential, and subsequent post-coating heat treatment. As a continuous length of fiber core is drawn through the sol, the coating process is effectively continuously repeated. Depending on the coating structure desired, after the fiber core is passed through a succession of sols and coated therewith, it may be drawn through a furnace, laser, or other controlled heat source, at appropriate temperatures for drying and curing. The process may be better understood from an examination of Figure 1, which illustrates the deposition of three coatings upon a fiber tow. It is to be noted that such a deposition process as illustrated may be used to provide any feasible number of layers, from 1 to as many as 100, if the individual layers are of a controlled thickness and the rate of application is properly controlled. For most purposes, however, the process of the present invention envisions the application of up to about 5 distinct successive layers of material upon a fiber core.

A conductive fiber core 10, from supply spool 12, is first cleaned (at cleaner 14) by a heat source, such as a laser or furnace, a chemical bath, or other suitable cleaning means, prior to contacting either a pair of or a single charging roller or pulley 20, which is electrically connected to variable DC power sources 21, 31, and 41. The fiber core thence passes through the sealing membrane 26 into the reservoir 25, and passes through the sol 27, and the annular electrode 22 immersed in the sol. It is noted that while the drawing illustrates a vertical

electrode/sol reservoir, it is possible to have the reservoir and electrode disposed horizontally, or at any appropriate angle, if proper provisions are made for dispersal of hydrogen resulting from the electrophoresis. The length of the electrode may be readily increased by this positioning, and may be extended to 20 feet or longer. It is also noted that the electrode within the reservoir need not be of the annular type, but may also be a flat plate, wire, or other suitable form immersed within the sol. After having been electrophoretically coated during passage through the annular electrode 22, the coated fiber core 28 passes from reservoir 25, and enters a second sol reservoir 35, having a membrane 36 at the lower end. The once coated fiber core, 28, passes through sol 37, and through the annular electrode 32 disposed therein, to receive a second coating. After passage through this second sol, which may be the same as or differ from the sol of reservoir 25, and deposition thereof on the fiber core, the fiber core, 38, which now bears two layers of coating material, is again withdrawn from the sol reservoir, and passes to a third sol reservoir, 45, containing another sol, 47, and annular electrode 42. This sol may be the same as, or differ from the sol or sols contained in reservoirs 25 and 35. However, prior to entry into reservoir 45, the twice coated fiber core, 38, passes through membrane 46. It has been found that it is appropriate to apply an increasing electrical potential between the fiber core and each successive annular electrode as the fiber passes through each successive reservoir, since each layer of material as it is applied to the fiber core acts as an insulator, decreasing the potential for deposition in the next sol. And, since the resistance of each such layer increases as the water and/or alcohol therein is removed, it is desirable that the coated fiber core travel rapidly throughout the coating system, so as to limit the amount of drying or curing of each layer of coating material before the next layer is applied.

The coated fiber core, 48, now bearing three layers of deposited metal oxide, is then passed through a drying furnace 50, to slowly eliminate water from the coatings. If this step is not carefully controlled, and if the coated fiber core is subjected to too rapid a heating, the release of steam from the initially applied sol, 27, may cause bubbles and/or voids in, or lifting of, the subsequently applied sols 37, and 47. After drying of the coated fiber core to a "green" state, the dry coated fiber core may now be passed through a curing furnace 52, to transform the coatings to their fully cured form. The furnaces are illustrated as being electric, with a single AC power source 54, but any form of heating source may be utilized. The coated fiber core may now be collected on collection spool 60. If the coating material has been deposited to a thickness greater than the fiber core, and constitutes a metal oxide, this may now appropriately be referred to as a metal oxide fiber. Alternatively, the fiber core may be removed, such as by dissolution by an acid, to produce a hollow metal oxide cylinder or fiber.

The fiber core may also, if carbon or carbon-based, be removed by heating in air at a sufficient temperature for sufficient time to result in complete oxidation.

Among the factors which contribute to the success of obtaining strongly adherent coatings are such variables as the number of layers to be applied, the specific coating materials employed, the degree of drying of the coated fiber between the time it leaves one sol and entry into the next, the extent of "wiping" of the coated fiber as it passes through the sealing membrane into the next reservoir in sequence, and the actual sequence of the materials. For example, some materials will bond together better than others, thus forming more adherent successive layers. For example, it has been found that a layer of alumina bonds very strongly to a layer of silicon carbide, but less adherently to an alumina fiber tow. Thus, one may desire to apply a layer of silicon carbide directly to an alumina tow prior to application of an alumina coating, to obtain the best bonding. The particulate sizes in successive layers may also be a factor. It has also been found that a layer of very fine particulate will bond well with a layer of slightly larger particulate, as a result of packing, or "filling in the voids" in the layer of larger particulates. As indicated previously, the coating materials may be applied in a sequence of differing sols, or as layers of the same material, as particulates of the same or differing sizes, in accordance with the requirements of the fiber to be produced. As an alternative, when a relatively porous final layer has been applied to a fiber core in accordance with the present invention, the coated fiber may be densified by the application of a slip of a suitable sol, such as a viscous silica sol, by such techniques as thermophoresis, spraying, dipping, etc., to locate smaller oxide particulate in the pores or voids of the applied coating so as to decrease the porosity thereof. Such an additional coating step may be performed, for example, either prior to or subsequent to entry of the fiber core into drying furnace 50. In addition, densification steps such as extruding the coated fiber may be performed to obtain a fully dense fiber.

Such apparatus as shown in Figure 1 is useful for the production of oxide coated fibers, dependent upon control of variables such as rate of fiber core passage through the annular electrode, applied potential at the electrode, density of the sol, and extent of hydrogen bubble removal measures. Such factors will effect the degree of success achieved in the preparation of defect-free, uniformly distributed, compact, and strongly adherent oxide coatings. The removal of hydrogen from the deposit is of particular importance, since its presence during the heating and drying steps results in creation of escape paths, and hence cracks in the coatings.

To decrease hydrogen evolution during electrophoresis, it has been found effective to limit the amount of water present in the sol subjected to electrophoresis, since the disassociation of water to hydrogen and oxygen is the source of bubbles which cause defects in the metal oxide layer deposited. One means to accomplish

this is to dewater, or concentrate the sol during preparation thereof, by evaporation of the water present to the greatest extent possible without causing the sol to gel, and then replacing such water in the sol by the addition of an alcohol, such as methanol, ethanol, isopropanol, butanol, etc. It is also noted that the choice of alcohol has a distinct effect upon the porosity of coatings formed by electrophoresis of the sol. Accordingly, one may choose to utilize a different alcohol if a more porous layer is desired. It has been found that in sols such as prepared as in Example 1, an alcohol to metal oxide molar ratio of above 50 is desirable, and that such sols are subject to markedly decreased hydrogen evolution during electrophoresis. Broadly, a molar ratio of alcohol to metal oxide of from about 50 to about 70 has been found effective, with a preferred range of from about 55 to about 69, and a more preferred range of from about 58 to about 67.

An alternative approach to hydrogen removal is to provide a continuous flow of air bubbles, or bubbles of an inert gas, to sweep the surface of the fiber core and the coating being deposited thereupon. The flow rate of these bubbles, which are preferably large relative to the size of the hydrogen bubbles formed by the electrophoresis, should exceed the rate of movement of the fiber core through the sol, so as to permit the air or inert gas to sweep away any hydrogen formed. The hydrogen is thereby carried to the surface of the sol or top of the electrophoresis cell, where it is released to the atmosphere, or evacuated. Such scrubbing bubbles may be generated in conventional fashion, or provided from a compressed gas source, to create an escape path for hydrogen gas at the point of separation of sol and coated fiber.

The rate of fiber core throughput also requires consideration and adjustment of electrical potential to achieve the coating thicknesses desired in individual layers. Low voltage results in less hydrogen evolution, but also requires a longer period of electrophoresis to attain a given thickness of deposit. Thicker layers may be achieved by either slowing the rate of fiber core passage, or lengthening the path through the annular electrode itself. Increased voltage, on the other hand, increases the rate of hydrogen evolution. Accordingly, the rates of fiber core throughput and coating voltage should be adjusted in accordance with the coating thicknesses desired and the specific sols, order of application, and fiber core employed. It has been found that potentials of from about 0.1 volt to about 100 volts or higher may be employed, preferably from about 1 to about 50 volts, and most preferably from about 35 to about 50 volts, with the fiber core subjected to a deposition period (i.e. the time of passage of a specified point on the fiber core through the length of the annular electrode) dependent upon the specific conductivity of the fiber core, the specific composition of the sol, and the voltage applied. Thus, the coating rate may vary greatly. For example, a fiber core may be coated by a YAG sol at a much faster rate of

fiber movement and a much lower voltage than the same fiber may be coated with an alumina sol. It is also to be noted that the potential and/or deposition time required for deposition of each sol subsequent to the first will be increased, due to the resistance of the layer of material deposited in the preceding deposition. As indicated, variation in the length of the annular electrode will also influence these factors, with a longer path permitting faster fiber core movement and/or lower voltages to achieve similar results. These parameters may be adjusted as desired.

It is noted that for purposes of obtaining defect-free, uniformly coated and strong multiple layer fibers, it is preferable to operate at throughput rates of from about 800 feet per hour (244 m per hour) to about 1600 feet per hour (488 m per hour), and voltages of from 35 to 100 volts, in the presence of a sweeping continuous flow of bubbles, thereby decreasing the formation of cracks or voids in the deposition resulting from the presence of hydrogen. To obtain the best quality fibers, electrophoresis at less than about 50 volts is recommended, although quite acceptable fibers may be obtained at potentials up to 100 volts, in the presence of a flow of scrubbing bubbles, dependent upon the specific sols and the rate of fiber core passage through the sols. The removal of hydrogen from the surface of the fiber core may also be aided by mechanical means, such as by vibration, including ultrasonic vibration of the sol, although these means are discouraged, since they also tend to lessen the adherence of successive layers to each other.

An additional factor in achieving successful deposition is the density of the particulate material in each sol, i.e. the availability of material for deposition. This may be influenced by recirculation of the sol in each reservoir to maintain a nearly constant concentration. Large sol holding tanks, not illustrated, may be utilized, with recirculating pumps to cause the flow of sol through the sol reservoirs 25, 35, and 45, with fresh sol added as appropriate to maintain the desired concentrations.

After passage through the final sol reservoir, the newly coated fiber core, bearing multiple deposits, must be dried. While forced hot air drying may be used, this approach is typically too slow and limiting for a continuous process. Preferably, the coated fiber core should be passed through a heated drying zone, such as a furnace, to remove any water and/or alcohol entrapped by the deposited particulate matter during electrophoresis. Control must be exercised, however, to avoid too rapid a heating and evolution of gaseous drying product, so as to prevent bubble formation and voids in the layered structure, as previously indicated. The dried, or so called "green" coated fiber must then be heated to an appropriate temperature to achieve complete transformation of the hydrates to the oxides. Dependent upon the time and temperature of this heating or curing step, one may control the degree of phase transformation to obtain specifically desired phases of alumina, yttria, or alumi-

na-yttria-garnet, for example, in the coated layers. The appropriate temperatures for curing are within the skill of the operator and may easily be determined, but temperatures from about 850°F (454°C) to about 1200°F (649°C) and above are appropriate for oxide formation. It is to be noted that in some instances, the fiber core per se is consumed during the curing process, after long periods at elevated temperature, resulting in a "free-standing" metallic oxide cylinder, tube, or jacket, i.e. an oxide fiber. Depending upon packing density, degree of phase transformation, thicknesses of oxide layers, etc., this fiber may exhibit varying degrees of flexibility, but in most instances may be wound upon a collection spool of approximately 4 inch diameter or greater. Such flexibility is of great value in the use of such fibers. For high speed commercial coating operations, it is also probable that a sizing layer, or non-carborizing sizing agent, will be applied to the coated fiber, by passage through a sizing tank, for example, to reduce fiber sticking and minimize damage to the fiber during winding and shipping.

It is also envisioned that sols of differing polarity may be applied to the fiber, as illustrated in Figure 2. It is to be noted that annular electrodes 22, 32, and 42 may be either cathodic or anodic, dependent upon the specific sols 27, 37, and 47, which are to be contacted in reservoirs 25, 35, and 45. Figure 2 demonstrates a possible configuration wherein the polarity of each annular electrode may be selected independently of the others, with appropriate connections made to charging rollers 20, 30, and 40, and isolated output variable DC sources 21, 31, and 41. In fact, reversing polarity between deposition of successive layers of coating material upon a relatively nonconductive fiber core, such as silicon carbide, may be found to increase the density and adherence thereof. Of course, the successive charging rollers, 30 and 40, would necessarily be carefully controlled relative to speed of rotation, and fashioned so as to contact the coated fiber in such a manner as to not remove the freshly applied coating from the previous sol reservoir, while still imparting the appropriate electrical charge thereto.

Coatings may be applied to various fiber cores in accordance with this invention, to produce multiple layer oxide fibers suitable for inclusion in metal matrix composites, wherein the multiple layer oxide fibers serve as reinforcement and/or strengthening inclusions.

Example 1

A coating line as illustrated in Figure 1 is used to apply a three layer coating of aluminum oxides to a 0.5 mil (12.7 μ m) diameter wire of tungsten - 3 percent rhenium alloy, using annular platinum anodes to electrophoretically deposit the layers. An alumina sol produced as set forth hereinabove is placed in reservoirs 25 and 45, while a sol comprising alumina doped with 3 weight percent chromium, also prepared in accordance with the exemplary method set forth hereinabove, is placed in

reservoir 35. Using the deposition process of this invention, a thin layer of alumina is first deposited on the fiber core, followed by a layer of chromium-doped alumina, and a final layer of alumina, at voltages of from 35 to 40 volts. The thusly coated fiber core is then dried at about 300°F (149°C) in an argon atmosphere, and subsequently cured at about 1200°F (649°C) in argon to a final oxide coated fiber having a total coating thickness of about 5 mils. When wound on a receiving spool, the applied coatings are strongly adherent and exhibit no visible porosity.

Example 2

A coating line as illustrated in Figure 2 is used to apply a three layer coating on a nonconductive sapphire fiber. The fiber is first made conductive by metallizing a thin layer of iron metal onto the fiber by chemical vapor deposition. Electrophoresis is conducted with platinum anodes 22 and 42, and a platinum cathode 32, to electrophoretically deposit layers of three different materials. An acidic alumina sol is placed in reservoir 25, a basic sol comprising zirconia and yttria is placed in reservoir 35, and an acidic YAG sol is placed in reservoir 45. The sols are prepared in accordance with the basic preparation method previously set forth. Using the process of this invention, a thin layer of alumina is first applied to the fiber, and the fiber passed to the second reservoir. The second layer is applied with the second power supply's output voltage reversed to make the platinum electrode cathodic, to deposit a thin layer of zirconia plus yttria. The third layer, YAG, is then applied using an annular platinum anode in the third reservoir. After deposition of the three layers, and drying and curing of the coated fiber, a strongly adherent three component coating is found on the fiber with no porosity or cracking visible.

Example 3

A coating line as illustrated in Figure 1 is used to apply a two layer coating of metal oxides to a 0.5 mil (12.7 µm) diameter wire of tungsten - 3 rhenium alloy, using annular platinum anodes to electrophoretically deposit the layers, followed by application of a protective overcoating of silica. An alumina sol produced as set forth hereinabove is placed in reservoir 25, a sol comprising zirconia, also prepared in accordance with the method set forth hereinabove, is placed in reservoir 35, and the two layers of oxide are deposited at voltages of about 60 volts, at a throughput rate of about 1000 feet per hour (305 m per hour). The coatings as applied are dried in an argon atmosphere at about 300 to 350°F (149 to 177°C), and then cured in argon at about 1200°F (649°C), in furnaces 50 and 52, respectively. After cooling, the coated wire is then coated by passage through a silica sol prepared from tetraethyl orthosilicate. The thusly silica coated fiber is then heated in an argon at-

mosphere drying furnace, and subsequently cured in an argon atmosphere to a final oxide coated fiber having a total coating thickness of about 5 mils. After collection, the applied coatings are strongly adherent and exhibit no visible cracking.

Example 4

A silicon carbide fiber core is coated with boron, by electrophoretic deposition from a sol, followed by application of an alumina coating in accordance with the invention as illustrated in Figure 1, using only two reservoirs. The fiber coating is targeted at 0.25 mils (6.4 µm) boron and 0.25-0.50 mils (6.4-12.7 µm) alumina. Processing speeds are controlled so as to yield the throughput times and temperatures of curing required to achieve a stable gamma or alpha alumina coating, depending on application.

Example 5

A silicon carbide fiber is coated with carbon, followed by a boron coating, both applied by electrophoretic deposition from a sol, in accordance with the invention. A chromium doped alumina coating is then applied by electrophoresis, with the coatings typically targeted at 0.25 mils (6.4 µm) boron, and 0.50-0.75 mils (12.7-19.1 µm) chromium-alumina. Processing speeds are selected so as to provide sufficient chromium-alumina for oxidation resistance.

Example 6

A boron fiber is electrophoretically coated with chromium doped alumina followed by application of a zirconia coating, in the manner set forth in Figure 1. The fiber coating is targeted at 0.1-0.25 mils (2.5-6.4 µm) thickness of chromium doped alumina followed by 0.5 mils (12.7 µm) zirconia. The final cure temperatures are above 1000°F (538°C) to stabilize the chromium doped alumina coating, and the zirconia sol has an yttria component of approximately 7-9 percent by weight.

Example 7

A tungsten fiber coated with carbon, applied electrophoretically, is then coated with an alumina layer, as illustrated in Figure 1, using only two electrophoresis deposition reservoirs, as in Example 4. Coating thicknesses are around 0.25 mils (6.4 µm) for the carbon, and 0.25-0.5 mil (6.4-12.7 µm) for the alumina. Since the carbon layer is conductive after drying, whereas metallic oxide coatings are not, this fiber may be subjected to drying after application of the carbon sol, and prior to application of the alumina. The processing temperature after carbon coating is between 300°F (149°C) and 500°F (260°C) to avoid carbonization before application of the alumina coating. After application of the alumina

coating, the coated fiber is heat treated at a temperature and time to allow for formation of stable gamma or alpha alumina phases, depending on the purpose for which the fiber is intended.

Claims

1. A method for depositing multiple coating layers upon a fiber core, comprising the steps of:

(a) electrophoretically depositing particulate material from a first sol onto an electrically conductive fiber core by applying a direct current potential between the fiber core and an oppositely charged electrode for sufficient time to obtain a uniform coating layer of the particulate material on the fiber core, wherein the first sol comprises water, an alcohol, and the particulate material selected from the group consisting of carbon, silicon, boron, boron nitride, alumina, zirconia, titania, chromium oxide, lanthanum oxide, hafnia, yttria, and mixtures thereof; (b) removing the coated fiber core from the sol; (c) repeating steps (a) and (b) at least one time with a subsequent sol to obtain a coated fiber core having at least two coating layers of particulate material, wherein the subsequent sol comprises water, an alcohol, and a particulate material selected as in step (a) and the particulate material in each subsequent sol differs from that of the preceding sol; (d) heating the coated fiber core to remove water and alcohol from the coating layers on the fiber core; (e) heating the coated fiber core at a temperature sufficient to cure the coating layers; and (f) recovering the cured coated fiber core.

2. The method of claim 1, wherein steps (a) and (b) are repeated at least twice with two subsequent sols to obtain a coated fiber core having at least three coating layers of particulate material.

3. The method of claim 1, wherein the direct current potential used to deposit the particulate material from each subsequent sol is higher than the direct current potential used to deposit the particulate material from the preceding sol.

4. The method of claim 1, wherein the direct current potential is about 35 volts to about 100 volts.

5. The method of claim 1, wherein the coated fiber core is heated in step (e) to a temperature of at least 454°C (850°F).

6. The method of claim 1, further comprising removing

hydrogen gas generated during step (a).

7. The method of claim 6, wherein the hydrogen gas is removed by flowing bubbles of air or an inert gas along the fiber core to sweep the hydrogen gas from the fiber core during electrophoresis.

8. The method of claim 1, further comprising applying a sizing layer over the coated fiber core after step (f).

9. The method of claim 1, further comprising the step of removing the fiber core from the coated fiber core after step (f).

10. The method of claim 1, wherein the fiber core is selected from the group consisting of fibers of aluminum, chromium, iron, molybdenum, nickel, niobium, rhenium, tantalum, titanium, tungsten, metallic alloys thereof, alumina, boron, carbon, cotton, glass, polyester, silicon carbide, silicon nitride, and wool.

11. The method of claim 1, wherein the particulate material in the sols of steps (a) and (c) is selected from the group consisting of alumina, zirconia, yttria, and mixtures thereof, and the fiber core is selected from the group consisting of fibers of silicon carbide, carbon, boron, and tungsten.

12. The method of claim 1, wherein the particulate material in sols of steps (a) and (c) is selected from the group consisting of oxides of aluminum, zirconium, titanium, chromium, lanthanum, hafnium, yttrium, and mixtures thereof; the particulate material is less than about 15 nm (150 Angstroms) in size; the molar ratio of alcohol to particulate material is about 50 to about 70; and the direct current potential is about 0.1 volts to about 100 volts.

13. The method of claim 1, wherein the alcohol in the sols of steps (a) and (c) is selected from the group consisting of methanol, ethanol, isopropanol, and butanol.

14. The method of claim 1, wherein the total thickness of the coating layers on the coated fiber core is equal to or greater than the diameter of the fiber core.

15. The method of claim 1, wherein the diameter of the coated fiber core of step (f) is about 7.6 μm (0.0003 inches) to about 229 μm (0.009 inches).

Patentansprüche

1. Verfahren zum Abscheiden von mehreren Beschichtungslagen auf einem Faserkern, folgend

Schritte aufweisend:

- (a) elektrophoretisch Abscheiden von teilchenförmigem Material aus einem ersten Sol auf einem elektrisch leitfähigen Faserkern durch Anlegen einer Gleichstromspannung zwischen dem Faserkern und einer entgegengesetzt geladenen Elektrode für eine zur Erhaltung einer gleichmäßigen Beschichtungslage aus dem teilchenförmigen Material auf dem Faserkern ausreichende Zeit, wobei das erste Sol Wasser, einen Alkohol und das teilchenförmige Material aufweist, das ausgewählt ist aus der Gruppe, die besteht aus Kohlenstoff, Silizium, Bor, Bornitrid, Aluminiumoxid, Zirkoniumdioxid, Titandioxid, Chromoxid, Lanthanoxid, Hafniumoxid, Yttriumoxid und Mischungen davon;
- (b) Entfernen des beschichteten Faserkerns aus dem Sol;
- (c) Wiederholen der Schritte (a) und (b) mindestens einmal mit einem nachfolgenden Sol, um einen beschichteten Faserkern mit mindestens zwei Beschichtungslagen aus teilchenförmigem Material zu erhalten, wobei das nachfolgende Sol Wasser, einen Alkohol und ein teilchenförmiges Material enthält, das ausgewählt ist wie in Schritt (a), und wobei sich das teilchenförmige Material in jedem nachfolgenden Sol von dem des vorausgehenden Sols unterscheidet;
- (d) Erwärmen des beschichteten Faserkerns, um Wasser und Alkohol aus den Beschichtungslagen auf dem Faserkern zu entfernen;
- (e) Erwärmen des beschichteten Faserkerns bei einer Temperatur, die zur Härtung der Beschichtungslagen ausreicht; und
- (f) Gewinnen des gehärteten beschichteten Faserkerns.
2. Verfahren nach Anspruch 1, bei dem die Schritte (a) und (b) mindestens zweimal mit zwei nachfolgenden Solen wiederholt werden, um einen beschichteten Faserkern mit mindestens drei Beschichtungslagen aus teilchenförmigem Material zu erhalten.
 3. Verfahren nach Anspruch 1, bei dem die zur Abscheidung des teilchenförmigen Materials aus jedem nachfolgenden Sol verwendete Gleichstromspannung höher ist als die zur Abscheidung des teilchenförmigen Materials aus dem vorausgehenden Sol verwendete Gleichstromspannung.
 4. Verfahren nach Anspruch 1, bei dem die Gleichstromspannung etwa 35 Volt bis etwa 100 Volt beträgt.
 5. Verfahren nach Anspruch 1, bei dem der beschichtete Faserkern in Schritt (e) auf eine Temperatur von mindestens 454°C (850°F) erwärmt wird.
 6. Verfahren nach Anspruch 1, außerdem aufweisend das Entfernen von während Schritt (a) erzeugtem Wasserstoffgas.
 7. Verfahren nach Anspruch 6, bei dem das Wasserstoffgas entfernt wird durch Strömenlassen von Blasen aus Luft oder einem Inertgas entlang des Faserkerns, um das Wasserstoffgas während der Elektrophorese von dem Faserkern zu spülen.
 8. Verfahren nach Anspruch 1, außerdem aufweisend das Aufbringen einer Versiegelungsschicht über dem beschichteten Faserkern nach Schritt (f).
 9. Verfahren nach Anspruch 1, außerdem aufweisend den Schritt des Entferns des Faserkerns von dem beschichteten Faserkern nach Schritt (f).
 10. Verfahren nach Anspruch 1, bei dem der Faserkern ausgewählt ist aus der Gruppe, die besteht aus Fasern aus Aluminium, Chrom, Eisen, Molybdän, Nickel, Niob, Rhenium, Tantal, Titan, Wolfram, Metalllegierungen davon, Aluminiumoxid, Bor, Kohlenstoff, Baumwolle, Glas, Polyester, Siliziumcarbid, Siliziumnitrid und Wolle.
 11. Verfahren nach Anspruch 1, bei dem das teilchenförmige Material in den Solen der Schritte (a) und (c) ausgewählt ist aus der Gruppe, die besteht aus Aluminiumoxid, Zirkoniumdioxid, Yttriumoxid und Gemischen davon, und bei dem der Faserkern ausgewählt ist aus der Gruppe, die besteht aus Fasern aus Siliziumcarbid, Kohlenstoff, Bor und Wolfram.
 12. Verfahren nach Anspruch 1, bei dem das teilchenförmige Material in den Solen der Schritte (a) und (c) ausgewählt ist aus der Gruppe, die besteht aus Oxiden von Aluminium, Zirkonium, Titan, Chrom, Lantan, Hafnium, Yttrium und Gemischen davon; das teilchenförmige Material weniger als etwa 15 nm (150 Angström) groß ist; das Molverhältnis von Alkohol zu teilchenförmigem Material etwa 50 bis etwa 70 beträgt; und die Gleichstromspannung etwa 0,1 Volt bis etwa 100 Volt beträgt.
 13. Verfahren nach Anspruch 1, bei dem der Alkohol in den Solen der Schritte (a) und (c) ausgewählt ist aus der Gruppe, die besteht aus Methanol, Ethanol, Isopropanol und Butanol.
 14. Verfahren nach Anspruch 1, bei dem die Gesamtdicke der Beschichtungslagen auf dem beschichteten Faserkern gleich dem Durchmesser des Faserkerns oder größer als der Durchmesser des Faserkerns ist.

15. Verfahren nach Anspruch 1, bei dem der Durchmesser des beschichteten Faserkerns von Schritt (f) etwa 7,6 μm (0,0003 Inch) bis etwa 229 μm (0,009 Inch) beträgt.

Revendications

1. Procédé pour déposer de multiples couches de revêtement sur un coeur de fibre, comprenant les étapes consistant à :

(a) déposer par électrophorèse un matériau particulaire à partir d'un premier sol sur un coeur de fibre électriquement conducteur en appliquant une tension continue entre le coeur de fibre et une électrode chargée avec une polarité opposée pendant un temps suffisant pour obtenir une couche de revêtement uniforme de matériau particulaire sur le coeur de fibre, dans lequel le premier sol contient de l'eau, un alcool et un matériau particulaire choisi dans le groupe formé de : carbone, silicium, bore, nitrure de bore, alumine, zircone, oxyde de titane, oxyde de chrome, oxyde de lanthane, oxyde d'hafnium, oxyde d'yttrium, et leurs mélanges ;
 (b) sortir du sol le coeur de fibres revêtu du sol ;
 (c) répéter les étapes (a) et (b), au moins une fois, avec un sol suivant pour obtenir un coeur de fibres revêtu ayant au moins deux couches de revêtement de matériau particulaire, dans lequel le sol suivant contient de l'eau, un alcool et un matériau particulaire, sélectionné comme à l'étape (a) et dans lequel le matériau particulaire de chaque sol suivant diffère de celui du sol précédent ;
 (d) chauffer le coeur de fibres revêtu pour éliminer l'eau et l'alcool des couches de revêtement déposées sur le coeur de fibre ;
 (e) chauffer le coeur de fibres revêtu à une température suffisante pour durcir les couches de revêtements ; et
 (f) récupérer le coeur de fibres revêtu durci.

2. Procédé selon la revendication 1, dans lequel les étapes (a) et (b) sont répétées, au moins deux fois, avec deux sols suivants pour obtenir un coeur de fibres revêtu ayant au moins trois couches de revêtement de matériau particulaire.

3. Procédé selon la revendication 1, dans lequel la tension continue, employée pour déposer le matériau particulaire à partir de chaque sol suivant, est supérieure à la tension continue utilisée pour déposer le matériau particulaire à partir du sol précédent.

4. Procédé selon la revendication 1, dans lequel la tension continue est d'environ 35 volts à environ

100 volts.

5. Procédé selon la revendication 1, dans lequel le coeur de fibres revêtu est chauffé à l'étape (e) jusqu'à une température d'au moins 464°C (850°F).

6. Procédé selon la revendication 1, comprenant encore l'étape consistant à extraire l'hydrogène gazeux généré pendant l'étape (a).

7. Procédé selon la revendication 6, dans lequel l'hydrogène gazeux est extrait en faisant circuler des bulles d'air ou un gaz inerte le long du coeur de fibre pour chasser l'hydrogène gazeux du coeur de fibre pendant l'électrophorèse.

8. Procédé selon la revendication 1, comprenant encore l'application d'une couche de calibrage par dessus le coeur de fibres revêtu après l'étape (f).

9. Procédé selon la revendication 1, comprenant encore l'étape qui consiste à sortir du coeur de fibres revêtu le coeur de fibre après l'étape (f).

10. Procédé selon la revendication 1, dans lequel le coeur de fibre est sélectionné parmi le groupe des fibres en : aluminium, chrome, fer, molybdène, nickel, niobium, rhénium, tantale, titane, tungstène, des alliages métalliques des métaux précédents, alumine, bore, carbone, coton, verre, polyester, carbure de silicium, nitrure de silicium et laine.

11. Procédé selon la revendication 1, dans lequel le matériau particulaire dans les sols des étapes (a) et (c) est sélectionné dans le groupe comprenant : alumine, zircone, oxyde d'yttrium, et leurs mélanges, et le coeur de fibre est sélectionné dans le groupe comprenant des fibres en carbure de silicium, carbone, bore et tungstène.

12. Procédé selon la revendication 1, dans lequel le matériau particulaire dans les sols des étapes (a) et (c) est sélectionné dans le groupe comprenant : des oxydes d'aluminium, zirconium, titane, chrome, lanthane, hafnium, yttrium et leurs mélanges, le matériau particulaire a au moins des dimensions d'environ 15 nm (150 Angströms) ; le rapport molaire entre l'alcool et le matériau particulaire est d'environ 50 à environ 70 ; et la tension continue est d'environ 0,1 volt à environ 100 volts.

13. Procédé selon la revendication 1, dans lequel l'alcool dans les sols des étapes (a) et (c) est sélectionné dans le groupe comprenant : méthanol, éthanol, isopropanol et butanol.

14. Procédé selon la revendication 1, dans lequel l'épaisseur totale des couches de revêtement sur le

coeur de fibres revêtu est égale ou supérieure au diamètre du coeur de fibre.

15. Procédé selon la revendication 1, dans lequel le diamètre du coeur de fibres revêtu de l'étape (f) est d'environ 7,6 μm (0.0003 pouce) à environ 229 μm (0.009 pouce).

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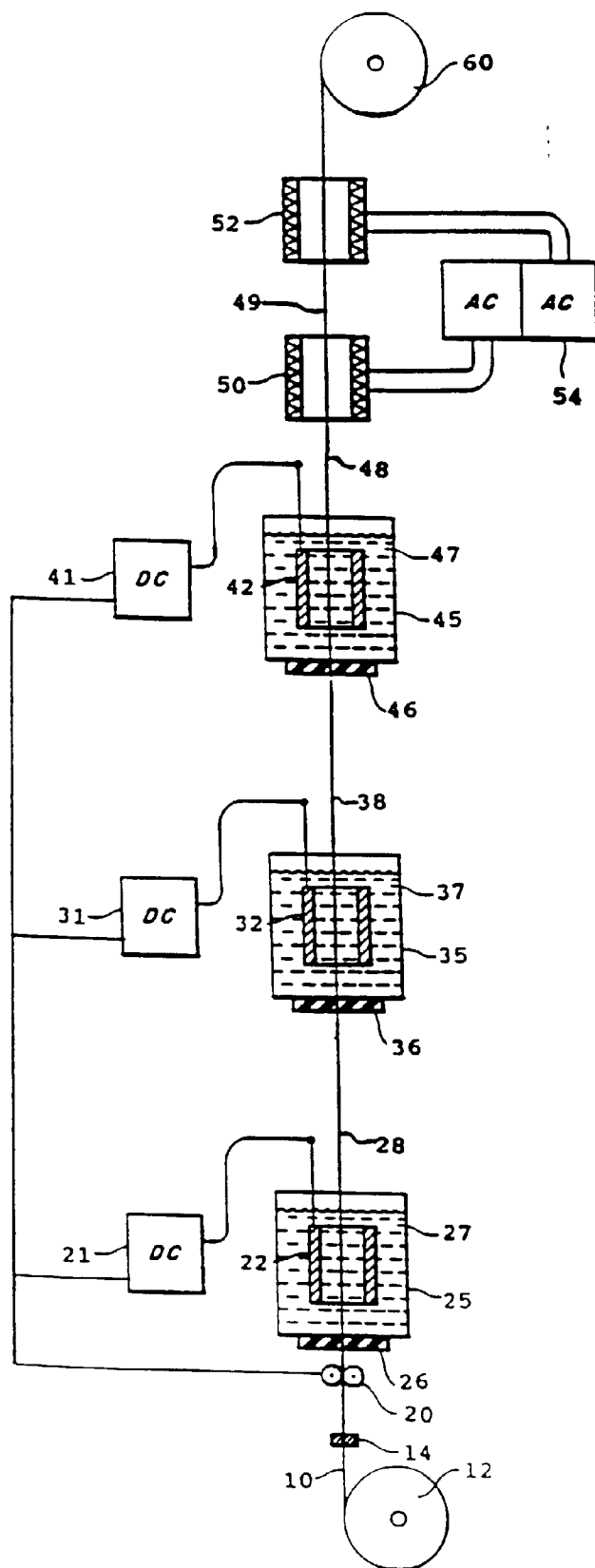


FIG. 1

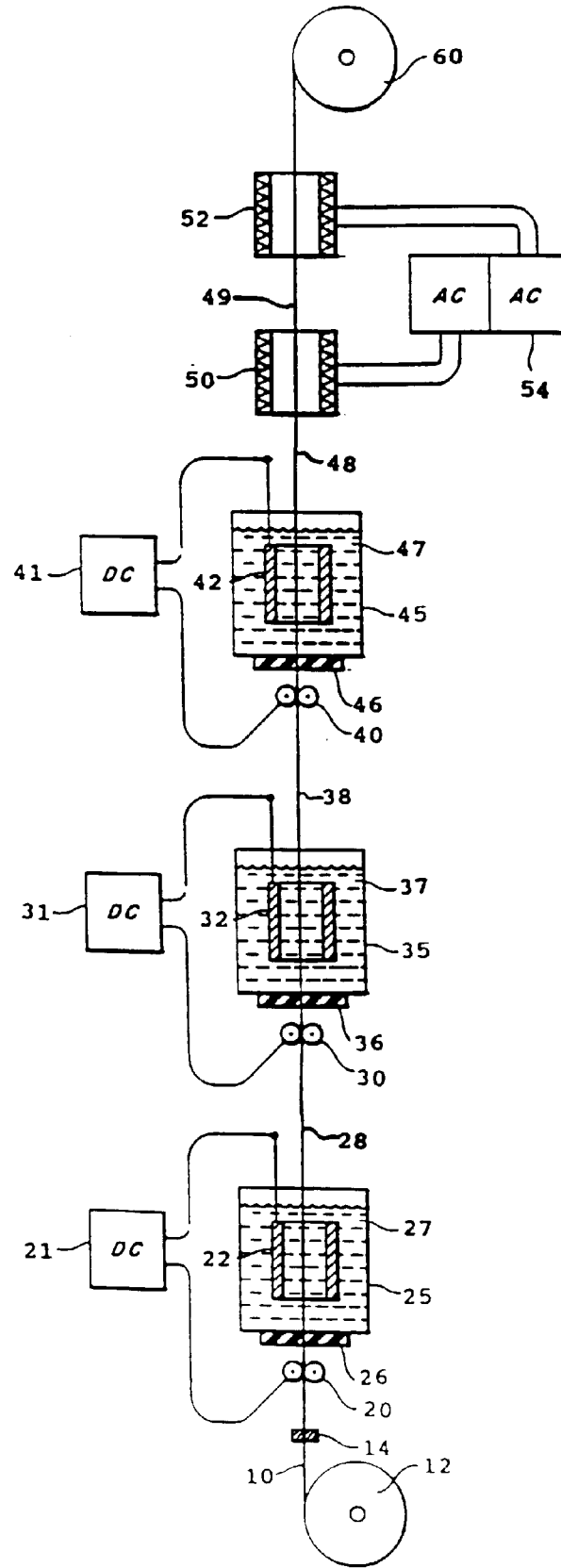


FIG. 2