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(54) Title: FIBERS, TUBES AND POROUS STRUCTURES OF METAL AND METAL OXIDE

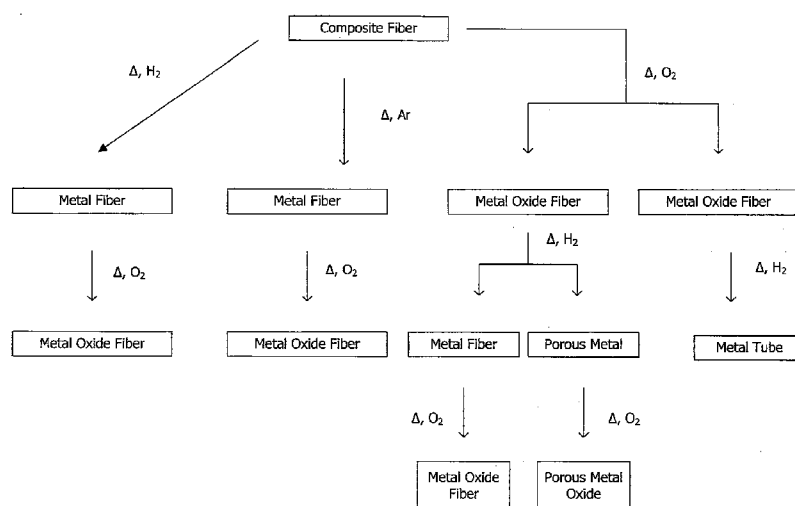


Figure 1

(57) Abstract: Nanoscale materials comprised of metal or metal oxide which are in the form of fibers or tubes or which have a porous structure can be prepared using composite fibers containing admixtures of polymers and metal precursors and/or metal oxide precursors.



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FIBERS, TUBES AND POROUS STRUCTURES OF METAL AND METAL OXIDE**CROSS-REFERENCE TO RELATED APPLICATION**

This application claims priority from United States provisional application 61/169766, filed April 16, 2009, and incorporated herein by reference in its entirety for all purposes.

5 **STATEMENT AS TO FEDERALLY SPONSORED RESEARCH**

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10 **BACKGROUND OF THE INVENTION**

This invention relates to materials, particularly nanoscale materials (i.e., structures having morphological features smaller than one-tenth of a micron in at least one dimension), comprised of metal or metal oxide which are in the form of fibers or tubes or which have a porous structure. The invention further pertains to processes for preparing
15 such materials from composite fibers comprised of admixtures of polymers and metal precursors or metal oxide precursors.

In recent years, there has been considerable interest in the preparation and use of so-called "nanoscale" materials such as nanofibers, nanowires, nanoparticles and the like as well as porous materials having very small pore sizes. Such materials have numerous
20 potential applications as supports, substrates, catalysts, electronic/electrical materials, composite components and so forth.

However, currently available methods for fabricating these materials are somewhat limited in their flexibility and it would be desirable to develop alternative preparation methods, including procedures which permit the synthesis of new nanoscale materials
25 that are different in composition and/or structure from previously known materials, procedures that are simpler and/or less costly than known techniques, as well as procedures that provide a greater degree of control over the structure and properties of the nanoscale materials obtained. For example, it would be useful to be able to easily adjust the grain or crystal size as well as the magnetic, electrical and optical properties
30 of the nanoscale materials.

SUMMARY OF THE INVENTION

The present invention provides a material selected from the group consisting of porous metals, porous metal oxides, metal oxide tubes, metal tubes, metal fibers, or metal oxide fibers, wherein said material has been produced by a process comprising heating a composite fiber comprised of an admixture of a polymer and a metal precursor or metal oxide precursor in an atmosphere selected from the group consisting of reducing atmospheres, inert atmospheres, and oxidizing atmospheres, subject to the proviso that said material is not a metal oxide fiber produced by heating a composite fiber comprised of a polymer and a metal oxide precursor in an oxidizing atmosphere and is not a metal fiber produced by heating a metal oxide fiber in a reducing atmosphere. Generally speaking, the composite fiber is heated at a temperature or temperatures within the range of from about 200 to about 700 degrees C, although as will be explained subsequently in further detail the heating protocol employed can be selected as desired to vary the structure and properties of the product thereby produced. Moreover, the characteristics of the product (grain/crystal size, morphology, metallic content, and so forth) may be readily varied and controlled by the type of atmosphere in which the heating is conducted or by first heating the composite polymer in one type of atmosphere and then heating the initial product thereby obtained in a different type of atmosphere.

In one aspect, the material is a porous metal obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber and b) heating said metal oxide fiber (e.g., at a temperature of at least about 450 degrees C) in a reducing atmosphere to form said porous metal.

In another aspect, the material is a porous metal oxide obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber, b) heating said metal oxide fiber in a reducing atmosphere to form a porous metal, and c) heating said porous

In another aspect, the material is a metal oxide tube obtained by heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form said metal oxide tube.

In another aspect, the material is a metal tube obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing

atmosphere to form a metal oxide tube and b) heating said metal oxide tube in a reducing atmosphere to form said metal tube.

In another aspect, the material is a metal fiber obtained by heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to
5 form the metal fiber.

In another aspect, the material is a metal fiber comprised of grains of metal and residual polymer and/or polymer decomposition products.

In another aspect, the material is a fiber comprised of metal grains separated by at least one substance selected from the group consisting of carbon, polymer, and polymer
10 decomposition products.

In another aspect, the material is a metal oxide fiber obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to form a metal fiber, and b) heating said metal fiber in an oxidizing atmosphere to form the metal oxide fiber.

15 Another aspect of the invention provides a process which comprises heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to form a metal fiber. Optionally, the metal fiber thus obtained may be heated in an oxidizing atmosphere to form a metal oxide fiber.

In another aspect, a process is provided which comprises:

- 20 a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber;
- b) heating said metal oxide fiber in a reducing atmosphere to form a porous metal; and, optionally
- c) heating said porous metal in an oxidizing atmosphere to form a porous metal
25 oxide.

In another aspect, a process is provided which comprises:

- a) heating a composite fiber comprised of an admixture of a first polymer and a metal oxide precursor in a first oxidizing atmosphere to form a first metal oxide tube; and, optionally
- 30 b) heating said metal oxide tube in a reducing atmosphere to form a metal tube; and, optionally

c) heating said metal tube in a second oxidizing atmosphere, which may be the same as or different from the first oxidizing atmosphere, to form a second metal oxide tube.

5 In another aspect, a method is provided for identifying combinations of polymers and metal oxide precursors that will be suitable for use in preparing a metal oxide tube in accordance with the process described in the previous paragraph. This method comprises:

- 10 a) subjecting i) a test sample of a selected polymer and a test sample of a selected metal oxide precursor or ii) a test sample of a mixture of said selected polymer and said selected metal oxide precursor to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with decomposition of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer and a second exothermic peak temperature
15 associated with complete decomposition of the polymer; and
- b) determining whether the first exothermic peak temperature and said second exothermic peak temperature are sufficiently distinct from each other, with said first exothermic peak temperature being lower than said second exothermic peak temperature, to permit a metal oxide tube to be prepared from a composite fiber
20 comprised of an admixture of said selected polymer and said selected metal oxide precursor by practice of the process described in the previous paragraph. In various embodiments of this aspect of the invention, the second exothermic peak temperature is at least 75 degrees C or at least 100 degrees C or at least 125 degrees C higher than the first exothermic peak temperature.

25 In another aspect, a method for determining conditions suitable for converting a composite fiber comprised of an admixture of a polymer and a metal oxide precursor to a metal oxide tube is provided. This method, which may usefully be practiced once a suitable polymer and a suitable metal oxide precursor have been identified and selected in accordance with the method described in the preceding paragraph, comprises:

- 30 a) subjecting i) a test sample of the polymer and a test sample of the metal oxide precursor or ii) a test sample of a mixture of the polymer and the metal oxide precursor or iii) a test sample of the composite fiber to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with
35 decomposition of the metal oxide precursor to metal oxide and/or oxidation of the

polymer to a partially decomposed polymer and a second exothermic peak temperature associated with complete decomposition of the polymer; and

b) selecting heat treatment conditions based on the first exothermic peak temperature and the second exothermic peak temperature measured in step a) effective to provide the metal oxide tube when the composite fiber is heated in an oxidizing atmosphere (for example, heating the composite fiber at a temperature that is higher than the first exothermic peak temperature but lower than the second exothermic peak temperature for a time effective to achieve at least partial crystallization of the metal oxide, before further heating the fiber to the second exothermic peak temperature).

In another aspect, a process is provided which comprises:

a) heating a composite fiber comprised of an admixture of a polymer and a metal precursor in a reducing atmosphere to form a metal fiber; and, optionally
b) heating said metal fiber in an oxidizing atmosphere to form a metal oxide fiber.

In another aspect, a process is provided which comprises:

a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in a first oxidizing atmosphere to form a first metal oxide fiber;
b) heating said first metal oxide fiber in a reducing atmosphere to form a metal fiber; and
c) heating said metal fiber in a second oxidizing atmosphere, which may be the same as or different from said first oxidizing atmosphere, to form a second metal oxide fiber.

In the foregoing aspect, the second metal oxide fiber may have an average metal oxide crystal size that is greater than the average metal oxide crystal size of the first metal oxide fiber. For example, the average crystal size in the second metal oxide fiber may be about the same as the diameter of the fiber. In one embodiment, the second metal oxide fiber may be a single crystal metal oxide fiber. Ordinarily, it is difficult to directly obtain metal oxide fibers having a relatively large average crystal size by heating a composite fiber in an oxidizing atmosphere. To increase crystal size in the metal oxide product obtained using such a process, it is generally necessary to use relatively high temperatures (e.g., in excess of 700 degrees C). However, such high temperatures tend to degrade the fiber structure (i.e., the product obtained may be non-fibrous). However, the temperature used in step c) of the process of this aspect of the present invention

may be much lower (e.g., within the range of from about 300 to about 400 degrees C), which is nonetheless effective to provide a relatively large crystal size while preserving the fibrous structure.

In another aspect, a method for determining conditions suitable for converting a metal oxide fiber into a metal fiber is provided. Such method comprises:

a) subjecting a test sample of said metal oxide fiber to analysis by differential scanning calorimetry in a reducing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with reduction of metal oxide in the metal oxide fiber to metal and a second exothermic peak temperature associated with grain growth and collapse of the fiber into a non-fibrous porous structure; and

b) selecting heat treatment conditions based on the first exothermic peak temperature and the second exothermic peak temperature measured in step a) effective to provide the metal fiber when the metal oxide fiber is heated in a reducing atmosphere (for example, selecting conditions such that the maximum temperature attained is less than the second exothermic peak temperature).

Still another aspect of the invention provides a process for producing a material selected from the group consisting of metal oxide tubes, metal tubes, metal fibers, or metal oxide fibers, wherein the desired product structure is secured by controlling the temperature experienced by the starting material during the process. This process comprises heating a composite fiber comprised of an admixture of a polymer and a metal precursor or metal oxide precursor in an atmosphere selected from the group consisting of reducing atmospheres, inert atmospheres, and oxidizing atmospheres, wherein during said heating said composite fiber is maintained in an environment capable of dissipating heat generated by exothermic reaction of said composite fiber (by placing the composite fiber in contact with a metal block, for example).

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 illustrates in schematic form some of the different products that can be obtained in accordance with the invention, as well as the different process steps that could be employed to produce such products.

DETAILED DESCRIPTION OF THE INVENTION

The fibers and tubes in accordance with the present invention can be obtained in the form of networks. The term "network" as used herein means a random or oriented

distribution of fibers or tubes in space that is controlled to form an interconnecting net (although the fibers or tubes need not be physically attached or bonded to one another). Where the network is comprised of a plurality of individual fibers or tubes, the individual fibers or tubes may be in contact with each other and/or interwoven or intertwined with each other. Where the network is comprised of a single continuous fiber or tube, such fiber or tube may be folded back, looped or otherwise configured such that multiple points along the fiber or tube are in contact with each other. The network may be three-dimensional; for example, the fiber or tube network may be in the form of a mat.

Among other materials, the present invention permits the fabrication of:

- a) metal oxide nanofibers having diameters within the range of 10 to 200 nm;
- b) metal oxide nanofibers comprised of nanograins having diameters within the range of 1 to 200 nm;
- c) magnetic metal oxide nanofibers comprised of exchange-coupled nanograins having diameters within the range of 1 to 40 nm;
- d) metal (metallic) nanofibers, including metal nanofibers having diameters within the range of 10 to 200 nm;
- e) metal nanofibers comprised of nanograins having diameters within the range of 1 to 200 nm;
- f) magnetic metal nanofibers comprised of exchange-coupled nanograins having diameters within the range of 1 to 40 nm;
- g) metal oxide nanotubes having outer diameters within the range of 30 to 200 nm and wall thicknesses within the range of 5 to 50 nm;
- h) metal oxide nanotubes comprised of nanograins having diameters within the range of 1 to 50 nm;
- i) metal nanotubes having outer diameters within the range of 30 to 200 nm and wall thicknesses within the range of 5 to 50 nm;
- j) porous metal structures;
- k) porous metal oxide structures; and
- l) single crystal metal oxide fibers.

Fibers in accordance with the invention may, for example, have diameters within the range of about 10 nm to several hundred nm, may contain single grains or crystals

(where, for instance, the diameter of the grain or crystal is approximately the same as the diameter of the fiber) or a plurality of nanograins or nanocrystals (having diameters much smaller than the fiber diameter), and may be magnetic or nonmagnetic. The magnetic interaction between magnetic grains can be readily tuned or adjusted by
5 controlling the grain size and the degree of separation of the grains.

The porous metals and porous metal oxides in accordance with the present invention are essentially non-fibrous in structure (i.e., individual fibers are not readily visible) and generally comprise interconnected three-dimensional strands having an open pore structure, with the diameters of the strands and pores typically being in the sub-micron
10 range (e.g., about 5 to about 500 nm).

The present invention utilizes composite fibers comprising at least one polymer and at least one metal precursor or metal oxide precursor, wherein such polymer(s) and metal precursor(s)/metal oxide precursor(s) are in admixture with each other. Such composite fibers are characterized by having the metal precursor or metal oxide precursor
15 distributed essentially throughout the fiber, not just deposited on the fiber surface.

In one aspect, the composite fibers are prepared by an electroprocessing method such as electrospinning. For example, a solution containing solvent, metal precursor or metal oxide precursor, and polymer (and/or polymer precursor) may be electrospun to form the composite fibers. Electrospinning is a technique well known in the art for forming
20 nanofibers containing metal precursors such as metal salts or metal compounds and is described, for example, in US 2008-0187996; WO 2007/022770; US 2008-0274403; and WO 2008/111960. Electrospinning involves atomization of a conducting fluid which exploits the interactions between an electrostatic field and the conducting fluid. During electrospinning, fibers with micron or sub-micron sized diameters are extruded by means
25 of an electrostatic potential from a polymer solution (see U.S. Pat. No. 1,975,504 to Formhals). When an external electrostatic field is applied to a conducting fluid (e.g., a semi-dilute polymer solution or a polymer melt), a suspended conical droplet is formed, whereby the surface tension of the droplet is in equilibrium with the electric field. Electrostatic atomization occurs when the electrostatic field is strong enough to
30 overcome the surface tension of the liquid. The liquid droplet then becomes unstable and a tiny jet is ejected from the surface of the droplet. As it reaches a grounded target, the material can be collected as an interconnected web containing relatively fine, i.e. small diameter, fibers.

Composite fibers useful in the present invention generally will have a diameter or thickness of 10 microns or less or, in one aspect, 1 micron or less. In particular aspects of the invention, the composite fibers have diameters of from about 10 to about 500 nm.

The selection of the polymer or polymer precursor can vary depending upon the metal precursor or metal oxide precursor used and the desired properties of the resultant composite fiber and derivatives subsequently prepared therefrom. Although not necessarily required, the polymer is generally a solid at room temperature. The selection of the polymer will also vary depending upon the solubility of the metal precursor or metal oxide precursor. As can be expected, the solubilities of metal oxide precursors and metal precursors can vary; however, one of ordinary skill in the art can select polymers that are compatible with the solvents used to dissolve the metal precursor or metal oxide precursor. Thus, it is possible to use water-soluble as well as water-insoluble polymers.

Among other factors to consider with respect to the polymer is its molecular weight. The molecular weight of the polymer used can influence the diameter of the electrospun fiber produced, for example. The molecular weight of the polymer can also influence the degree of solubility a polymer has in a given solvent system, the solution viscosity, and surface tension. The solution viscosity is an important factor with respect to electrospun fiber formation, in that if the solution viscosity is too great, it will not result in the formation of a random arrangement of fibers. Conversely, if a solution of metal oxide and polymer is not sufficiently viscous, "beaded" fibers or droplets will form.

Alternatively, one or more polymer precursors can be used to produce the polymer *in situ*. The polymer precursor is any compound capable of undergoing polymerization. Depending upon the functional groups present on the polymer precursor, the precursor can undergo polymerization via a number of different mechanisms. For example, the polymer precursor can be a polyisocyanate, which can react with a polyamine or a polyol (e.g., diamine or diol, respectively, each of which can also be considered a polymer precursor) to produce a polymer *in situ*. The polymer precursor can also include other materials used to make condensation polymers including polyesters, polyamides, and polycarbonates. It is also contemplated that a polymer and a polymer precursor can be used in combination, where the two components may or may not react with one another. In one aspect, the polymer precursor can polymerize during electrospinning to form a polymer *in situ*.

In other aspects, the polymer comprises one or more functional groups capable of interacting with the metal precursor or metal oxide precursor. Examples of functional

groups include, but are not limited to, hydroxyl, amino, carboxyl, and the like.

Depending upon the metal precursor/metal oxide precursor and functional group present on the polymer, the interaction between the metal precursor/metal oxide precursor and polymer can result in the formation of covalent or non-covalent bonds.

- 5 In one aspect, the polymer is selected from among the following types of polymers (including mixtures thereof): polystyrenes (including copolymers of vinyl aromatic monomers with one or more other types of monomers), polyacrylates, polyimides, polyethers (e.g., polypropylene oxides, polyethylene oxides), polysulfones, polystyrenesulfonic acids, polyethyleneimines, polyvinyl alcohols, polyvinylformals, polyoxazalines, polyvinylpyridines, polysaccharides, polyamides, polyvinylalkylethers, cycloolefinic copolymers, polymethylmethacrylates, polyesters (e.g., polyethylene terephthalate), polymethacrylates, polyurethanes, polyolefins (e.g., polypropylenes, polyethylenes, copolymers of ethylene and/or propylene with higher alpha-olefins), polycarbonates, fluoropolymers, cellulosic polymers, polylactic acids, polylactide-co-glycolides, polycaprolactones, polyacrylamides, polysulfonates, polyketones, polyacrylonitriles, polymethylpentenes, polyvinylpyrrolidinones (polyvinylpyrrolidones), and polyvinyl acetates. The polymer may be thermoplastic, elastomeric, thermoset, or thermosettable and may be linear, branched or cross-linked. Copolymers of different monomers, including random, block, tapered and grafted copolymers, may be employed.
- 20 Polymers that are soluble in polar solvents are utilized in one aspect of the invention.

The term "metal precursor" as used herein is defined as any non-metallic compound containing at least one metal atom and at least one non-metal atom that is capable of being converted to metallic form (either directly or indirectly). Similarly, the term "metal oxide precursor" as used herein is defined as any non-metallic compound containing at least one metal atom and at least one non-metal atom that is capable of being converted to a metal oxide (such as through an oxidation or decomposition reaction). Suitable metal atoms include, but are not limited to, Sn, Ti, Ni, Fe, Co, Cu, Zn, In, Zr, Mo, W, Al, Mn, Pb, V, Cr, Ru, Hf, Ta, Ce and the like and combinations thereof. As will be clear from the following description, a particular compound such as a metal nitrate can function as both a metal precursor and a metal oxide precursor in the context of the present invention, depending upon the processing conditions to which it is subjected.

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In one aspect, the metal oxide precursor or metal precursor is selected from the group consisting of metal salts, metal alkoxides, metal hydroxides, metal carboxylates (metal esters, such as metal acetates), metal nitrides, metal carbides, metal halides (e.g., metal chlorides), metal sulfides, metal selenides, metal phosphates, metal sulfates,

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metal carbonates, metal nitrates, metal nitrites, or a combination thereof. The metal oxide precursor or metal precursor may contain more than one type of component in addition to the metal atoms (e.g., the metal oxide precursor or metal precursor may be a metal nitrate/chloride). The precursor may contain organic groups or may be completely inorganic. Specific illustrative examples of suitable metal precursors and metal oxide precursors include metal salts such as iron nitrate, nickel nitrate, cobalt nitrate, copper nitrate, tungsten nitrate, zinc nitrate, tin nitrate, zirconium nitrate, molybdenum nitrate, aluminum nitrate, manganese nitrate, lead nitrate, vanadium nitrate, chromium nitrate, ruthenium nitrate, hafnium nitrate, tantalum nitrate, cerium nitrate and titanium nitrate as well as the corresponding acetates and chlorides. Mixtures or combinations of different metal oxide precursors and/or metal precursors may be utilized. The metal oxide precursor or metal precursor may contain more than one type of metal atom.

Typically, it will be desirable to employ a composite fiber containing a significant amount of metal precursor or metal oxide precursor relative to the amount of polymer. For example, the composite fiber may be comprised of about 30 to about 70 weight percent metal precursor/metal oxide precursor and about 30 to about 70 weight percent polymer.

Preferably, a solvent or mixture of solvents is employed for the preparation of the polymer solution to be subjected to electrospinning which is capable of solubilizing both the polymer and the metal precursor/metal oxide precursor. This helps to ensure that the metal precursor/metal oxide precursor is substantially evenly and homogeneously distributed throughout the polymeric matrix of the composite fiber. The choice of solvent or solvents will depend upon the characteristics of the polymer and metal precursor/metal oxide precursor starting materials which are selected, as well as the desired concentrations of each. Suitable solvents can include, for example, water, alcohols (e.g., aliphatic alcohols such as methanol, ethanol, isopropanol, butanol, aromatic alcohols such as benzyl alcohols), carboxylic acids (e.g., acetic acid), amines, glycols (e.g., diethylene glycol), amides (e.g., dimethylformamide, dimethylacetamide), sulfoxides (e.g., dimethylsulfoxide), halogenated hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons and the like and mixtures thereof. In one embodiment of the invention, dimethylformamide is used as a solvent or cosolvent. The use of DMF and other polar, organic solvents containing one or more nitrogen and/or oxygen atoms is especially preferred, as such solvents are believed to be especially effective in coordinating with the metal precursor or metal oxide precursor and thus dissolving them into solution with the polymer at relatively high concentrations.

As mentioned previously, the composite fibers as well as derivatives thereof are heated (annealed) in different types of atmospheres in order to control the type of product thereby obtained. The term "oxidizing atmosphere" as used herein means an atmosphere capable of effecting the decomposition or oxidation of a substrate to yield a metal oxide, for example, the decomposition of a metal nitrate to the corresponding metal oxide or the oxidation of a metal to the corresponding metal oxide. Any of the oxidizing agents known in the art can be used for such purpose, but for cost and convenience reasons it will generally be preferred to employ an atmosphere comprising oxygen (O₂) such as air, oxygen-enriched air, or a synthetically prepared mixture of an inert gas like nitrogen with an oxidizer such as oxygen. Other oxidizing agents such as ozone or the like could also be used. The term "inert atmosphere" as used herein means an atmosphere which by itself is incapable of effecting either the oxidation or reduction of a metal oxide precursor or metal precursor. The inert atmosphere thus may, for example, consist essentially of or consist of one or more inert gases such as argon, helium, nitrogen or the like. The term "reducing atmosphere" as used herein means an atmosphere capable of effecting the reduction of an oxidized metal species such as a metal oxide or metal salt to the corresponding metal. Hydrogen (H₂) is an example of a suitable reducing agent, although for cost and safety reasons it may be desirable to dilute the hydrogen with one or more inert gases.

As will be explained in more detail in the examples that follow, the present invention is exceptionally flexible and versatile and many different types of useful nanoscale materials can be readily obtained by controlling the choice of starting materials as well as the processing conditions (in particular, temperature and the type of atmosphere to which the starting material is subjected while being heated).

For example, when a composite fiber comprised of an admixture of a polymer and a metal oxide precursor is heated in an oxidizing atmosphere, either a metal oxide fiber or a metal oxide tube can be obtained, depending upon the characteristics of the particular polymer and metal oxide precursor which are selected as well as the manner in which the heating is carried out. To successfully convert a composite fiber into a metal oxide tube (rather than a metal oxide fiber), we have found that the metal oxide precursor should be capable of being converted into a metal oxide at a temperature lower than the temperature at which the polymer undergoes complete decomposition. Typically, it will be preferred if these temperatures are distinct and well-separated (e.g., decomposition or oxidation of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer takes place at a temperature at which no major polymer decomposition occurs). Differential scanning calorimetry may be usefully

employed for the purpose of identifying combinations of polymers and metal oxide precursors that can be utilized to prepare composite fibers that will be capable of being converted by heating in an oxidizing atmosphere to tubular metal oxide structures. For example, the following method can be practiced:

- 5 a) subjecting i) a test sample of a selected polymer and a test sample of a selected metal oxide precursor or ii) a test sample of a mixture of said selected polymer and said selected metal oxide precursor to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with oxidation or
10 decomposition of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer and a second exothermic peak temperature associated with complete decomposition of the polymer; and
- 15 b) determining whether the first exothermic peak temperature and said second exothermic peak temperature are sufficiently distinct from each other, with said first exothermic peak temperature being lower than said second exothermic peak temperature, to permit a metal oxide tube to be prepared from a composite fiber comprised of an admixture of said selected polymer and said selected metal oxide precursor by practice of the process described in the previous paragraph.

For a particular combination of polymer and metal oxide precursor to be suitable for use
20 in preparing a composite fiber that can be converted into a metal oxide tube by heating in an oxidizing atmosphere, the second exothermic peak temperature preferably is at least 75 degrees C or at least 100 degrees C or at least 125 degrees C higher than the first exothermic peak temperature. The rate of temperature increase employed in the ramped heating program can be varied as desired so as to control the width of the
25 observed exothermic peaks in the DSC curve (thereby achieving better resolution or separation of the peaks, for example) and, to some extent (within a relatively narrow range), the peak temperatures. For instance, if the rate of temperature increase is relatively fast, the exothermic peak associated with conversion of the metal oxide precursor into a metal oxide may be broadened (i.e., spread out over a wider
30 temperature range) causing it to overlap to a significant extent with the exothermic peak associated with polymer decomposition, even when the peak temperatures (the temperatures at which maximum exotherms are observed) are otherwise well separated.

In addition to selecting polymer and metal oxide precursor combinations that by DSC analysis have well-separated exothermic peak temperatures, we have also found that
35 careful control of the heating conditions to which the composite fiber containing the

selected polymer and metal oxide precursor combination helps to ensure that a metal oxide tube structure is obtained when the composite fiber is heated in an oxidizing atmosphere. If the composite fiber is simply exposed to or heated quickly to a temperature in excess of the temperature at which the metal oxide precursor is converted to a metal oxide and at least equal to the temperature at which substantial, rapid decomposition of the polymer takes place, a metal oxide fiber (having a solid structure) generally is obtained. If, however, the composite fiber is subjected to a suitable rate of temperature increase between the temperature at which metal oxide formation takes place and the temperature at which rapid and complete polymer decomposition occurs, then it is possible to instead obtain a metal oxide tube (i.e., a cylindrical metal oxide structure having a hollow core). Differential scanning calorimetry (DSC) may be employed to select the reaction conditions that will be effective to convert a particular composite fiber to a metal oxide tube structure. For example, the following method can be practiced:

- a) subjecting a test sample of a composite fiber comprised of an admixture of a polymer and a metal oxide precursor to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with decomposition or oxidation of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer and a second exothermic peak temperature associated with complete decomposition of the polymer; and
- b) selecting heat treatment conditions based on the first exothermic peak temperature and the second exothermic peak temperature measured in step a) effective to provide the metal oxide tube when the composite fiber is heated in an oxidizing atmosphere.

Once the exothermic peak temperatures have been determined, the conditions under which the composite fiber should be annealed in order to convert it to a metal oxide tube are selected such that the fiber is slowly heated within the temperature range between the exothermic peak temperatures or is held at a temperature within that range for a relatively long period of time before eventually being heated to a temperature effective to completely decompose the polymer. The annealing conditions should be chosen so as to permit the metal oxide precursor to form a metal oxide shell (which may also include crystallization of the metal oxide) prior to full polymer decomposition. In a preferred embodiment of the invention, the heating conditions are selected using differential scanning calorimetry such that the exothermic peaks are distinct and well-separated

(i.e., conversion of the metal oxide precursor to metal oxide is essentially completed before any significant decomposition of the polymer begins to take place).

It should be noted that, because of the typically high surface/mass ratio of the fibers, the heat released in the initial exothermic reaction (associated with the metal oxide precursor decomposition/oxidation and/or oxidation of the polymer to a partially decomposed polymer) may have a significant effect on the temperature of a fiber sample. In some cases, conventional ramping rate control methods are sometimes not sufficient to avoid having the local temperature of the sample exceed (overshoot) the set temperature. Such overheating will effectively merge the two isothermal peaks in controlled DSC experiments, which means that the reactions (the metal oxide precursor oxidation/decomposition reaction, the partial oxidation of the polymer and the complete polymer decomposition reaction) effectively happen at the same time. As a result, a tube structure will generally not be achieved under such conditions. In the event that the conventionally-controlled ramping rate is for this reason ineffective to provide a tube structure, the sample can instead be contacted with (e.g., bonded to) a metal block to increase the thermal mass. The metal block helps to quickly dissipate the heat generated in the exothermic reaction into the environment. Alternatively, the flow rate of air (or other oxidation gas) over the sample can be controlled so as to effectively dissipate the heat into the environment.

Similar techniques may be utilized so as to provide better control over the temperatures a particular sample may experience during processing in accordance with any aspect of this invention, thereby influencing the structure and characteristics of the product thereby obtained. That is, while heating a sample of a composite fiber or a derivative thereof (i.e., an intermediate product obtained from the composite fiber), such sample is maintained in an environment capable of dissipating heat generated by exothermic reaction of the composite fiber or derivative thereof, thereby limiting the maximum temperature experienced by the sample.

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the invention.

EXAMPLES

Preparation of Stock Solutions for Electrospinning

Stock solutions of polyvinylpyrrolidinone (PVP) prepared by dissolving 0.5 g PVP in 10 mL of a mixture of isopropanol (5 mL) and dimethylformamide (5 mL), then adding the desired amount of metal salt(s). For example, to prepare an iron nitrate stock solution, 0.5 g $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is added. To prepare composite fibers containing NiFeO_4 , 0.18 g nickel nitrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 0.5 g iron nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ are added to form the stock solution.

Electrospinning

The stock solutions are used in an electrospinning process to manufacture composite fibers containing PVP and one or more metal salts. A 34 gauge needle is attached to a plastic pipe connected to a 10 mL syringe holding the stock solution. The needle is electronically attached to a power supply setting at ca. 10-15 KV. The needle is suspended so that the tip of the needle is held vertically ca. 8-12 cm above an electrically grounded collecting cylinder drum that can rotate at various speeds, with a layer of aluminum foil covering the cylinder surface. A flow rate controller feeds the stock solution at a rate of ca. 0.3-0.6 mL/h. Composite fibers having diameters of from about 60 to 400 nm can be produced in this manner, with the fiber diameter being tuned by varying the bias voltage, collecting distance, solution flow rate and solution concentration. The as-spun fiber is collected on the aluminum foil covering the drum. The entire set-up is placed in a glove box having a humidity controlled at 20%, as the humidity of the environment during electrospinning can affect the formation and quality of the as-spun fibers. Alignment of the as-spun fiber can be achieved simply by rotating the collection drum at very high speed, yielding randomly oriented and aligned as-spun fiber.

Preparation of Metal Oxide Fibers

After the electrospinning process is completed, the aluminum foil containing the collected composite fibers is removed from the drum, placed in a furnace and heated at a temperature of 450-550 degrees C in air for 1 to 2 hours. During this process, the polymer in the composite fibers is selectively removed and the remaining metal salt is converted to crystallized metal oxide fibers having tunable diameters of 10 to 200 nm. The grain size within each fiber can be controlled within the range from 1 to 20 nm. Grain size can be measured by x-ray diffraction (XRD) using the Scherrer equation and by TEM/SEM imaging, both of which are well-known methods in the field. Where the metal oxide obtained is a complex metal oxide such as NiFe_2O_4 (i.e., where the oxide contains more than one type of metal atom), the first heating (annealing) is generally effective to provide a metal oxide fiber with controllable fiber diameter and grain size.

The metal oxide fibers formed a fibrous network resembling a thin film that could be peeled off the aluminum foil substrate.

The grain size of fibers containing complex metal oxides could be modified by subjecting the initially obtained metal oxide fibers to a second heating (annealing) step.

5 **Preparation of Metal Oxide Tubes**

By carefully tuning the parameters used to anneal the composite fibers such as the annealing temperature, the ramping rate (the rate at which the annealing temperature is increased), and the thermal mass (by attaching the composite fiber sample to a metal block, for example), homogeneous metal oxide tubes having outer diameters of 30 to 10 200 nm can be fabricated.

Differential scanning calorimetry (DSC) was used to examine the thermal behavior of an electrospun fiber comprised of PVP and iron nitrate. A DSC curve was obtained by heating the fiber in air to 500 degrees C in a Perkin Elmer DSC-7 using a ramping rate of 20 degrees C/min. Separate annealing of additional samples of the same fiber was also 15 carried out to different maximum temperatures at the same ramping rate, with the samples being cooled down immediately after reaching the pre-selected maximum temperature. A fiber sample was first annealed to a maximum temperature of 384 degrees C (which is between the two major exothermic peaks observed when a fiber sample is heated to 500 degrees C), then cooled down and again annealed, this time to a 20 maximum temperature of 500 degrees C. When overlapped, the two DSC curves observed resemble the DSC curve obtained when a fiber sample is heated directly from 30 to 500 degrees C. This suggests that the reaction which results in the first exothermic peak observed by DSC is a non-reversible process and does not affect the reaction which results in the second exothermic DSC peak.

25 The samples obtained at different maximum annealing temperatures were examined by transmission electron microscopy (TEM) high resolution imaging and x-ray photoelectron spectroscopy (XPS). When heated up to 384 degrees C (after exhibiting the first exothermic reaction), the inner structure of the heated fiber was similar to that of the as-spun fiber when examined by TEM; that is, no apparent contrast was observable across 30 the diameter of the fiber. However, a high resolution TEM image showed that there were small clusters of crystallization evenly distributed within the fiber, which is consistent with the formation of a Fe_2O_3 phase as suggested by the XPS data. Once the fiber was heated to a temperature in excess of the second exothermic DSC peak, the inner structure of the fiber exhibited a significant change. Between 384 degrees C and 410

degrees C, the diameter of the fiber shrunk by about one half. A core-shell contrast started to become visible at a temperature over 410 degrees C. When the temperature reached 470 degrees C, a tube structure (i.e., a tubular structure having a hollow core) was clearly evident.

5 Other composite fibers were studied using the same procedures. These results demonstrated that as long as the DSC curve exhibited two distinct exothermic peaks (as had been observed for the PVP/Fe(NO₃)₃ fiber), a tube structure could be obtained. It is believed that the two exothermic peaks indicate that the oxidation/decomposition of the metal salt and the crystallization of the resulting metal oxide take place before the
10 polymer is removed. Cobalt oxide (Co₃O₄) and nickel iron oxide (NiFe₂O₄) nanotubes were successfully prepared by the aforescribed annealing process. However, when a PVP/Ni(NO₃)₃ composite fiber was employed, attempts to obtain a metal oxide tube structure were unsuccessful. When examined by DSC, such a fiber exhibits an oxidation/decomposition peak at a temperature that is too close to the temperature at
15 which PVP removal (decomposition) takes place.

Preparation of Metal Fibers

Metal oxide fibers prepared as described above were placed in a quartz glass bottle, which was then positioned in a furnace and subjected to a second heat treatment at a temperature of from 300 to 450 degrees C for 1 hour in a reducing atmosphere (5%
20 hydrogen, 95% argon). Extensive studies were performed using DSC, XRD (x-ray diffraction), SEM (scanning electron microscopy), TEM, and EDAX (energy dispersive spectroscopy) characterization methods to examine the effect of processing conditions on the product thereby obtained. The first exothermic peak in the DSC curve was found to be associated with the reduction of the metal oxide into pure metal, whereas the second
25 exothermic peak was found to be due to grain growth and the collapse of the fiber into a non-fibrous porous structure. Therefore, in order to obtain a metal fiber, the annealing temperature had to be selected to be between the peak temperatures at which the exotherms were observed. Once the reduction of the metal oxide into metal was completed, metal fiber having a diameter of about 60 nm was obtained. The quartz
30 bottle was immediately sealed to prevent oxidation of the metal fiber.

Preparation of Porous Metal

As previously mentioned, metal oxide fibers could be transformed into a material having a porous metal structure by heating the fibers at a relatively high temperature (450 to 600 degrees C) in a reducing atmosphere (5% hydrogen, 95% argon).

5 Preparation of Porous Metal Oxide

The porous metal materials described previously could be converted into materials having a porous metal oxide structure by heating the porous metal materials in the presence of oxygen (i.e., in an oxidizing atmosphere).

Direct Preparation of Metal Fiber

10 The as-spun composite fibers containing PVP and metal nitrate were directly converted into metal fibers by heating at 500 degrees C for 1 hour in an inert atmosphere (argon).

For example, the DSC curve of a composite fiber containing cobalt nitrate (20 degrees C/min heating rate) exhibits two exothermic peaks at about 230 degrees C and about 280 degrees C. It is believed that these two peaks are attributable to the partial
15 decomposition of the PVP. A broad endothermic peak is also observed at about 450 degrees C, which is thought to be associated with the reduction of the cobalt nitrate to metallic cobalt by the decomposed PVP acting as a reducing agent. Most of the PVP was apparently burned off by heating to 500 degrees C, although some amount of carbon appeared to be retained in the fibers (with the residual carbon separating metal grains).
20 The amount of residual carbon as well as the degree of metal separation could be tuned by adjusting the annealing temperature and the duration of the time the fiber was maintained in the 450 to 500 degree C temperature range.

Further annealing (heating) of the metal fibers was found to be capable of changing the grain separation (by controlled removal of the residual polymer) and the grain size. For
25 example, a metal fiber sample prepared using an initial annealing temperature (in an inert atmosphere) of 490 degrees C exhibited an average grain size of 5 nm, but when this sample was annealed again (in an inert atmosphere) at 550 degrees C the metal fiber product obtained was found to have an average grain size of 11 nm. Generally, the temperature of the second annealing determines the maximum grain size (i.e., when the
30 sample is held at a particular set temperature, the grain size will typically reach a maximum value; to further increase the grain size, it will usually be necessary to raise the temperature at which the sample is heated). The length of time the sample is held at a temperature higher than the polymer decomposition temperature generally determines the amount of residual polymer. The polymer can be completely removed, if

desired, by extended heating at a temperature at least equal to the polymer decomposition temperature, yielding pure metal fiber. For magnetic materials, the grain separation and grain size will affect the magnetic interaction between the grains and thus the overall electromagnetic properties of the metal fiber material. Because of the ability to retain some polymer or polymer decomposition products in the fiber, metal fibers made by the aforescribed procedure (conversion of a composite polymer/metal precursor fiber directly to the metal fiber) tend to exhibit greatly improved mechanical properties as compared to metal fibers prepared by a two step process in which the composite fiber is first converted to a metal oxide fiber and the metal oxide fiber is then reduced to a metal fiber). In particular, the metal fibers obtained by direct conversion have improved flexibility and do not break easily, despite being less than 1 micron thick. Using such a method also provides good control of the magnetic properties of the metal fiber by tuning grain size and separation, which can lead to significant changes in the magnetic interaction between metal grains within the fiber. This facilitates adjustment of the magnetic properties of the metal fiber. The electrical transport properties can also be modified by adjusting the size of the metal grains and the extent to which the metal grains are separated from each other. Additionally, metal fibers produced by this procedure have enhanced chemical stability.

What is claimed is:

1. A material selected from the group consisting of porous metals, porous metal oxides, metal oxide tubes, metal tubes, metal fibers, or metal oxide fibers, wherein said material
5 has been produced by a process comprising heating a composite fiber comprised of an admixture of a polymer and a metal precursor or metal oxide precursor in an atmosphere selected from the group consisting of reducing atmospheres, inert atmospheres, and oxidizing atmospheres, subject to the proviso that said material is not a metal oxide fiber produced by heating a composite fiber comprised of a polymer and a metal oxide
10 precursor in an oxidizing atmosphere and is not a metal fiber produced by heating a metal oxide fiber in a reducing atmosphere.
2. A material according to Claim 1, wherein said material is a porous metal obtained by
15 a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber and b) heating said metal oxide fiber in a reducing atmosphere to form said porous metal.
3. A material according to Claim 1, wherein said material is a porous metal oxide
20 obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber, b) heating said metal oxide fiber in a reducing atmosphere to form a porous metal, and c) heating said porous metal in an oxidizing atmosphere to form the porous metal oxide.
4. A material according to Claim 1, wherein said material is a metal oxide tube obtained
25 by heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form said metal oxide tube.
5. A material according to Claim 1, wherein said material is a metal tube obtained by a)
30 heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide tube and b) heating said metal oxide tube in a reducing atmosphere to form said metal tube.

6. A material according to Claim 1, wherein said material is a metal fiber obtained by heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to form the metal fiber.

5 7. A material according to Claim 1, wherein said material is a metal oxide fiber obtained by a) heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to form a metal fiber, and b) heating said metal fiber in an oxidizing atmosphere to form the metal oxide fiber.

10 8. A material according to Claim 1, wherein said composite fiber has been obtained by electrospinning.

9. A material according to Claim 1, wherein said composite fiber has been obtained by electrospinning using a solution of said polymer and said metal precursor or metal oxide
15 precursor.

10. A material according to Claim 1, wherein said metal precursor or metal oxide precursor is a metal salt.

20 11. A material according to Claim 1, wherein said metal precursor or metal oxide precursor is a metal nitrate, metal halide or metal carboxylate.

12. A material according to Claim 1, wherein said metal precursor or metal oxide precursor is at least one salt of at least one metal selected from the group consisting of
25 cobalt, iron, nickel, copper, titanium, tungsten, zinc, vanadium, chromium, manganese, zirconium, ruthenium, hafnium, tantalum and cerium.

13. A material according to Claim 1, wherein said polymer is a polyvinylpyrrolidone.

30 14. A material according to Claim 1, wherein said material is a metal tube, metal oxide tube, metal fiber or metal oxide fiber having a diameter of less than 1 micron.

15. A material according to Claim 1, wherein said material is a metal tube, metal fiber or porous metal consisting essentially of metal.

5 16. A material according to Claim 1, wherein said material is a metal tube, metal fiber or porous metal consisting essentially of at least one metal selected from the group consisting of cobalt, iron, nickel, copper, titanium, tungsten, zinc, vanadium, chromium, manganese, zirconium, ruthenium, hafnium, tantalum and cerium.

10 17. A material according to Claim 1, wherein said material is a metal oxide tube, metal oxide fiber or porous metal oxide consisting essentially of metal oxide.

18. A material according to Claim 1, wherein said material is a metal oxide tube, metal oxide fiber or porous metal oxide consisting essentially of at least one metal oxide
15 selected from the group consisting of iron oxides, cobalt oxides, nickel oxides, copper oxides, titanium oxides, tungsten oxides, zinc oxides, vanadium oxides, chromium oxides, manganese oxides, zirconium oxides, ruthenium oxides, hafnium oxides, tantalum oxides, cerium oxides and mixtures thereof.

20 19. A material according to Claim 1, wherein said material is a metal fiber comprised of grains of metal and residual polymer and/or polymer decomposition products.

20. A fiber comprised of metal grains separated by at least one substance selected from the group consisting of carbon, polymer, and polymer decomposition products.

25

21. A process, comprising:

a) heating a composite fiber comprised of an admixture of a polymer and a metal precursor in an inert atmosphere to form a metal fiber.

30 22. The process of Claim 21, wherein said inert atmosphere is comprised of nitrogen, argon, or mixtures thereof.

23. The process of Claim 21, wherein said heating is carried out within a temperature range of from about 425 to about 575 degrees C.

5 24. The process of Claim 21, additionally comprising:

b) heating said metal fiber in an oxidizing atmosphere to form a metal oxide fiber.

25. A process, comprising:

10 a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide fiber; and
b) heating said metal oxide fiber in a reducing atmosphere to form a porous metal.

15 26. A process in accordance with Claim 25, additionally comprising:

c) heating said porous metal in an oxidizing atmosphere to form a porous metal oxide.

27. A process, comprising:

20 a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in an oxidizing atmosphere to form a metal oxide tube.

28. A process in accordance with Claim 27, additionally comprising:

b) heating said metal oxide tube in a reducing atmosphere to form a metal tube.

25

29. A process, comprising:

a) heating a composite fiber comprised of an admixture of a polymer and a metal precursor in a reducing atmosphere to form a metal fiber.

30 30. A process in accordance with Claim 29, additionally comprising:

b) heating said metal fiber in an oxidizing atmosphere to form a metal oxide fiber.

31. A process in accordance with Claim 30, wherein the metal oxide fiber is a single
5 crystal metal oxide fiber.

32. A process, comprising:

- a) heating a composite fiber comprised of an admixture of a polymer and a metal oxide precursor in a first oxidizing atmosphere to form a first metal oxide fiber;
- 10 b) heating said first metal oxide fiber in a reducing atmosphere to form a metal fiber; and
- c) heating said metal fiber in a second oxidizing atmosphere, which may be the same as or different from said first oxidizing atmosphere, to form a second metal oxide fiber.

15

33. A process in accordance with Claim 32, wherein the second metal oxide fiber has an average metal oxide crystal size that is greater than that of the first metal oxide fiber.

34. A process in accordance with Claim 32, wherein the second metal oxide fiber is a
20 single crystal metal oxide fiber.

35. A method for determining conditions suitable for converting a composite fiber comprised of an admixture of a polymer and a metal oxide precursor to a metal oxide tube, said method comprising:

- 25 a) subjecting a test sample of said composite fiber to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with decomposition or oxidation of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer and a second exothermic peak temperature associated with complete decomposition of the polymer; and
- 30 b) selecting heat treatment conditions based on the first exothermic peak temperature and the second exothermic peak temperature measured in step a)

effective to provide the metal oxide tube when the composite fiber is heated in an oxidizing atmosphere.

36. A method in accordance with Claim 35, wherein said test sample is in contact with a metal block when being heated, said metal block being capable of dissipating at least a portion of the heat generated by said test sample during the analysis.

37. A method for determining conditions suitable for converting a metal oxide fiber into a metal fiber, said method comprising:

- a) subjecting a test sample of said metal oxide fiber to analysis by differential scanning calorimetry in a reducing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with reduction of metal oxide in the metal oxide fiber to metal and a second exothermic peak temperature associated with grain growth and collapse of the fiber into a non-fibrous porous structure; and
- b) selecting heat treatment conditions based on the first exothermic peak temperature and the second exothermic peak temperature measured in step a) effective to provide the metal fiber when the metal oxide fiber is heated in a reducing atmosphere.

38. A method for identifying combinations of polymers and metal oxide precursors that will be suitable for use in preparing a metal oxide tube in accordance with the process of claim 27, said method comprising:

- a) subjecting i) a test sample of a selected polymer and a test sample of a selected metal oxide precursor or ii) a test sample of a mixture of said selected polymer and said selected metal oxide precursor to analysis by differential scanning calorimetry in an oxidizing atmosphere using a ramped heating program to measure a first exothermic peak temperature associated with oxidation or decomposition of the metal oxide precursor to metal oxide and/or oxidation of the selected polymer to a partially decomposed polymer and a second exothermic peak temperature associated with complete decomposition of the polymer; and
- b) determining whether the first exothermic peak temperature and said second exothermic peak temperature are sufficiently distinct from each other, with said first exothermic peak temperature being lower than said second exothermic peak temperature, to permit a metal oxide tube to be prepared from a composite fiber

comprised of an admixture of said selected polymer and said selected metal oxide precursor by practice of the process of claim 27.

39. A process for producing a material selected from the group consisting of metal oxide
5 tubes, metal tubes, metal fibers, or metal oxide fibers, said process comprising heating a
composite fiber comprised of an admixture of a polymer and a metal precursor or metal
oxide precursor or a derivative of said composite fiber in an atmosphere selected from
the group consisting of reducing atmospheres, inert atmospheres, and oxidizing
atmospheres, wherein during said heating said composite fiber or derivative thereof is
10 maintained in an environment capable of dissipating heat generated by exothermic
reaction of said composite fiber or derivative thereof.

40. A process in accordance with claim 39, wherein said composite fiber or derivative
thereof is in contact with a metal block during said heating.

15

41. A process in accordance with claim 39, wherein said heating is performed using a
differential scanning calorimeter.

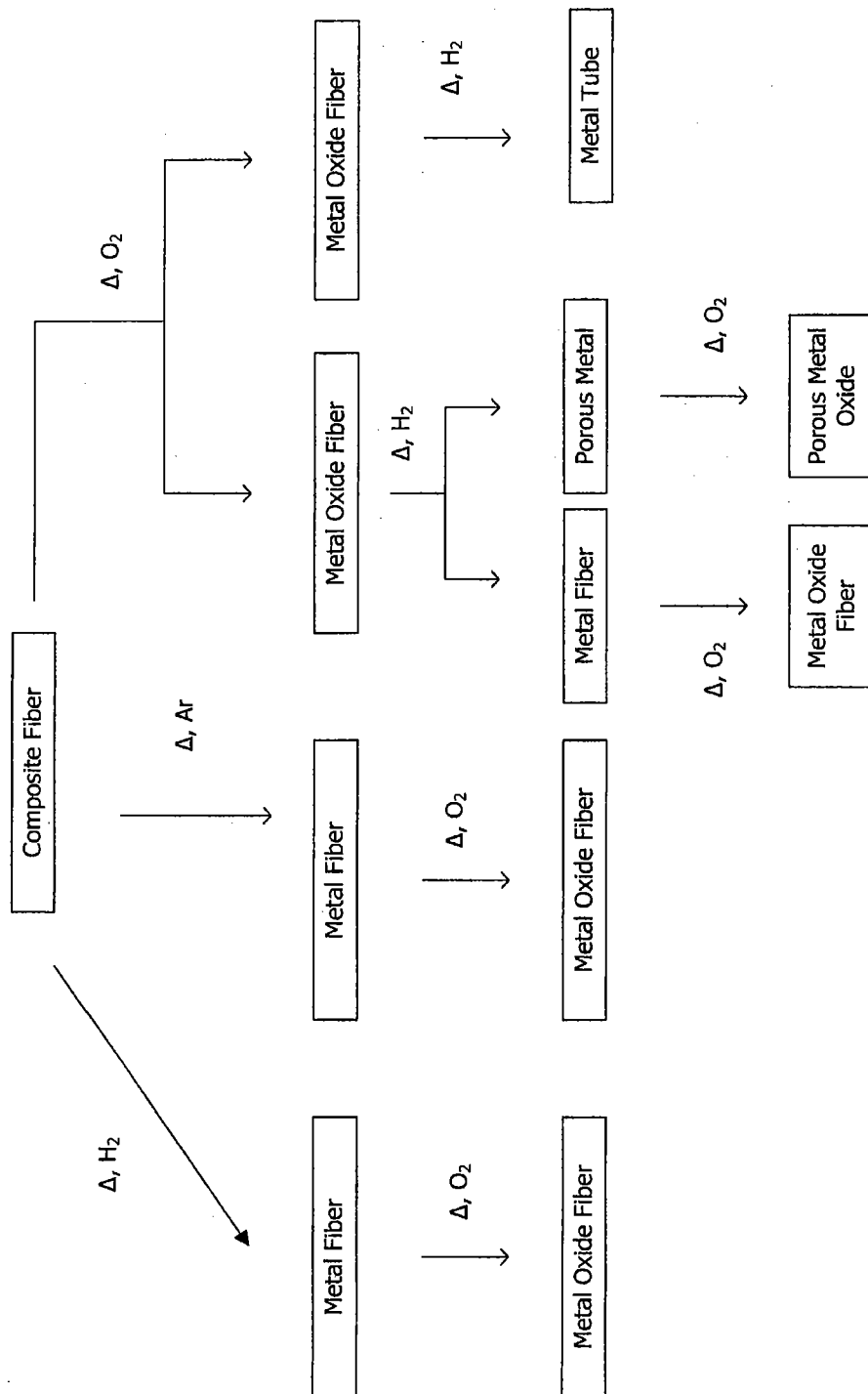


Figure 1