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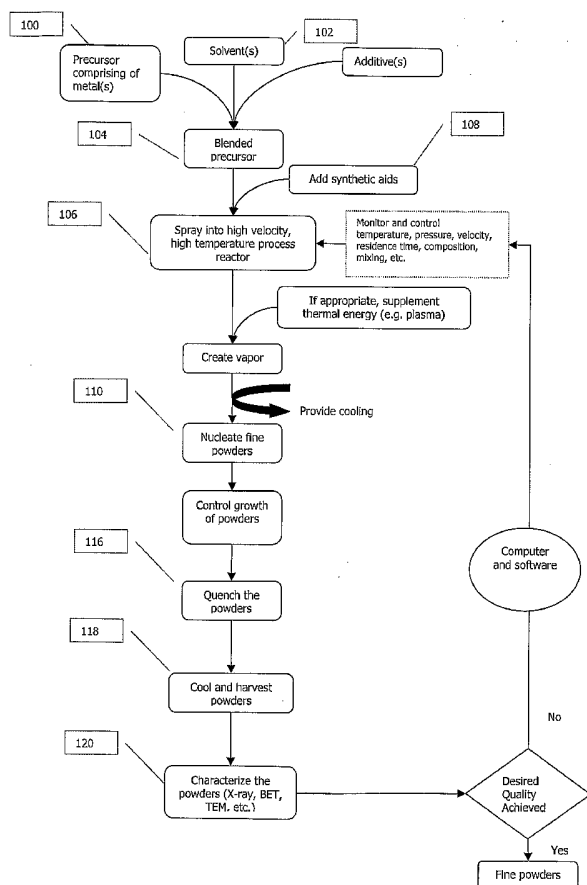
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(54) Title: NANOMATERIALS MANUFACTURING METHODS AND PRODUCTS THEREOF

(57) Abstract: Methods for manufacturing nanomaterials and related nanotechnology are provided.





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NANOMATERIALS MANUFACTURING METHODS AND PRODUCTS THEREOF

CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

This application is a continuation-in-part of U.S. patent application 09/790,036, filed on Feb. 20, 2001, and is a continuation-in-part of U.S. patent application 10/755,024, filed on Jan. 09, 2004. The present application claims the benefit of provisional application number 60/568,132, filed May 4, 2004. Each of these three applications is
5 hereby incorporated by reference in its entirety.

The present invention generally relates to methods of manufacturing submicron and nanoscale powders.

Powders are used in numerous applications. They are the building blocks of electronic, telecommunication, electrical, magnetic, structural, optical, biomedical,
10 chemical, thermal, and consumer goods. On-going market demands for smaller, faster, superior and more portable products have demanded miniaturization of numerous devices. This, in turn, demands miniaturization of the building blocks, i.e. the powders. Sub-micron and nano-engineered (or nanoscale, nanosize, ultrafine) powders, with a size 10 to 100 times smaller than conventional micron size powders,
15 enable quality improvement and differentiation of product characteristics at scales currently unachievable by commercially available micron-sized powders.

Nanopowders in particular and sub-micron powders in general are a novel family of materials whose distinguishing feature is that their domain size is so small that size confinement effects become a significant determinant of the materials' performance.
20 Such confinement effects can, therefore, lead to a wide range of commercially important properties. Nanopowders, therefore, are an extraordinary opportunity for design, development and commercialization of a wide range of devices and products for various applications. Furthermore, since they represent a whole new family of material precursors where conventional coarse-grain physiochemical mechanisms are
25 not applicable, these materials offer unique combinations of properties that can enable

novel and multifunctional components of unmatched performance. Yadav et al. in a co-pending and commonly assigned U.S. Patent Application No. 09/638,977, which along with the references contained therein is hereby incorporated by reference in its entirety, teach some applications of sub-micron and nanoscale powders.

5 Some of the challenges in the cost-effective production of powders involve controlling the size of the powders as well as controlling other characteristics, such as the shape, distribution, and composition of the powder. Thus, innovations are desired in the production of sub-micron powders in general and nanoscale powders in particular, which allow the control of the characteristics of the powders produced.

10 Briefly stated, the present invention provides methods for manufacturing nanoscale powders comprising a desired metal. The present invention also provides applications of nanoscale powders.

In some embodiments, the present invention provides nanoparticles comprising doped or undoped metal oxides.

15 In some embodiments, the present invention provides composites and coatings comprising doped or undoped metal oxides.

In some embodiments, the present invention provides applications of powders comprising doped or undoped metal oxides.

20 In some embodiments, the present invention provides methods for producing novel nanoscale powders comprising metals in high volume, low-cost, and reproducible quality with control of various powder characteristics.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows an exemplary overall approach for producing submicron and nanoscale powders in accordance with the present invention.

DETAILED DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

The present invention is generally directed to very fine inorganic powders. The scope of the teachings includes high purity powders. Powders discussed herein are of mean crystallite size less than 1 micron, and in certain embodiments less than 100 nanometers. Methods for producing and utilizing such powders in high volume, low-cost, and reproducible quality are also provided.

Definitions

For purposes of clarity the following definitions are provided to aid the understanding of the description and specific examples provided herein. Whenever a range of values are provided for a specific variable, both the upper and lower limit of the range are included within the definition.

“Fine powders” as used herein, refers to powders that simultaneously satisfy the following criteria:

- (1) particles with mean size less than 10 microns; and
- (2) particles with aspect ratio between 1 and 1,000,000.

For example, in some embodiments, the fine powders are powders that have particles with a mean domain size less than 5 microns and with an aspect ratio ranging from 1 to 1,000,000.

“Submicron powders” as used herein, refers to fine powders with a mean size less than 1 micron. For example, in some embodiments, the submicron powders are powders that have particles with a mean domain size less than 500 nanometers and with an aspect ratio ranging from 1 to 1,000,000.

The terms “nanopowders,” “nanosize powders,” “nanoparticles,” and “nanoscale powders” are used interchangeably and refer to fine powders that have a mean size less than 250 nanometers. For example, in some embodiments, the nanopowders are powders that have particles with a mean domain size less than 100 nanometers and with an aspect ratio ranging from 1 to 1,000,000.

Pure powders, as the term used herein, are powders that have composition purity of at least 99.9% by metal basis. For example, in some embodiments the purity is 99.99%.

Nanomaterials, as the term used herein, are materials in any dimensional form (zero, one, two, three) and domain size less than 100 nanometers.

- 5 “Domain size,” as that term is used herein, refers to the minimum dimension of a particular material morphology. In the case of powders, the domain size is the grain size. In the case of whiskers and fibers, the domain size is the diameter. In the case of plates and films, the domain size is the thickness.

- The terms “powder,” “particle,” and “grain” are used interchangeably and encompass, for example, oxides, carbides, nitrides, borides, chalcogenides, halides, metals, intermetallics, ceramics, polymers, alloys, and combinations thereof. These terms include single metal, multi-metal, and complex compositions. These terms further include hollow, dense, porous, semi-porous, coated, uncoated, layered, laminated, simple, complex, dendritic, inorganic, organic, elemental, non-elemental, composite, doped, undoped, spherical, non-spherical, surface functionalized, surface non-functionalized, stoichiometric, and non-stoichiometric forms or substances. Further, the term powder in its generic sense includes one-dimensional materials (fibers, tubes, etc.), two-dimensional materials (platelets, films, laminates, planar, etc.), and three-dimensional materials (spheres, cones, ovals, cylindrical, cubes, monoclinic, parallelolipids, dumbbells, hexagonal, truncated dodecahedron, irregular shaped structures, etc.). The term metal used above includes any alkali metal, alkaline earth metal, rare earth metal, transition metal, semi-metal (metalloids), precious metal, heavy metal, radioactive metal, isotopes, amphoteric element, electropositive element, cation forming element, and includes any current or future discovered element from the periodic table excluding non-metals.
- 10
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20
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“Aspect ratio,” as the term is used herein, refers to the ratio of the maximum to the minimum dimension of a particle.

“Precursor,” as the term is used herein, encompasses any raw substance that can be transformed into a powder of the same or different composition. In certain

embodiments, the precursor is a liquid. The term precursor includes, but is not limited to, organometallics, organics, inorganics, solutions, dispersions, melts, sols, gels, emulsions, or mixtures.

“Powder,” as the term is used herein, encompasses oxides, carbides, nitrides, chalcogenides, metals, alloys, and combinations thereof. The term includes hollow, dense, porous, semi-porous, coated, uncoated, layered, laminated, simple, complex, dendritic, inorganic, organic, elemental, non-elemental, dispersed, composite, doped, undoped, spherical, non-spherical, surface functionalized, surface non-functionalized, stoichiometric, and non-stoichiometric forms or substances.

“Coating” (or “film” or “laminate” or “layer”), as the term is used herein, encompasses any deposition comprising submicron and nanoscale powders. The term includes in its scope a substrate, surface, deposition, or a combination thereof that is hollow, dense, porous, semi-porous, coated, uncoated, simple, complex, dendritic, inorganic, organic, composite, doped, undoped, uniform, non-uniform, surface functionalized, surface non-functionalized, thin, thick, pretreated, post-treated, stoichiometric, or non-stoichiometric form or morphology.

“Dispersion,” as the term is used herein, encompasses inks, pastes, creams, lotions, Newtonian, non-Newtonian, uniform, non-uniform, transparent, translucent, opaque, white, black, colored, emulsified, with additives, without additives, water-based, polar solvent-based, or non-polar solvent-based mixture of powder in any fluid or fluid-like state of substance.

In some embodiments, the present invention is directed to submicron and nanoscale powders comprising doped or undoped metal oxides. Given the relative abundance of metal in the earth’s crust and current limitations on purification technologies, it is expected that many commercially produced materials would have naturally occurring metal impurities. These impurities are expected to be below 100 parts per million and in most cases in a concentration similar to other elemental impurities. Removal of such impurities does not materially affect the properties of interest to an application. For the purposes herein, powders comprising metal impurities wherein the impure

metal is present in a concentration similar to other elemental impurities are not considered powders comprising metals for the purposes this invention. However, it is emphasized that in one or more doped or undoped compositions of matter, certain metal may be intentionally engineered as a dopant into a powder at concentrations of
5 100 ppm or less, and these are included in the scope of this invention.

In a generic sense, the present invention teaches nanoscale powders, and in a more generic sense, submicron powders comprising at least 100 ppm by weight of a metal, in some embodiments greater than 1 weight % by metal basis, and in other embodiments greater than 10 weight % by metal basis.

10 FIG. 1 shows an exemplary overall approach for the production of submicron powders in general and nanopowders in particular. The process shown in FIG. 1 begins with a metal containing raw material (for example, but not limited to, coarse oxide powders, metal powders, salts, slurries, waste products, organic compounds, or inorganic compounds). Figure 1 shows one embodiment of a system for producing
15 nanoscale and submicron powders in accordance with the present invention.

The process shown in Figure 1 begins at 100 with a metal-containing precursor such as an emulsion, fluid, particle-containing fluid suspension, or water-soluble salt. The precursor may be evaporated metal vapor, evaporated alloy vapor, a gas, a single-phase liquid, a multi-phase liquid, a melt, a sol, a solution, a fluid mixture, a solid
20 suspension, or combinations thereof. The metal-containing precursor comprises a stoichiometric or a non-stoichiometric metal composition with at least some part in a fluid phase. Fluid precursors are utilized in certain embodiments of this invention. Typically, fluids are easier to convey, evaporate, and thermally process, and the resulting product is typically more uniform.

25 In one embodiment of this invention, the precursors are environmentally benign, safe, readily available, high-metal loading, lower-cost fluid materials. Examples of metal-containing precursors suitable for the purposes of this invention include, but are not limited to, metal acetates, metal carboxylates, metal ethanoates, metal alkoxides, metal octoates, metal chelates, metallo-organic compounds, metal halides, metal

azides, metal nitrates, metal sulfates, metal hydroxides, metal salts soluble in organics or water, ammonium comprising compounds of the metal, and metal-containing emulsions.

In another embodiment, multiple metal precursors may be mixed. Mixtures of precursors can be useful, if complex nanoscale and submicron powders are desired. For example, a calcium precursor and a titanium precursor may be mixed to prepare calcium titanium oxide powders for electroceramic applications. As another example, a cerium precursor, a zirconium precursor, and gadolinium precursor may be mixed in correct proportions to yield a high purity, high surface area, mixed oxide powder for ionic device applications. In yet another example, a barium precursor (and/or zinc precursor) and a tungsten precursor may be mixed to yield powders for pigment applications. Such complex nanoscale and submicron powders can be used to create materials with surprising and unusual properties not available through the respective single metal oxides or a simple nanocomposite formed by physically blending powders of different compositions. An illustration of such an unusual property is the refractive index of nanoscale aluminum silicate powder which can be varied by changing the aluminum and silicon ratio of the composition. The refractive index so achievable is not available through either aluminum oxide or silicon oxide or a simple nanocomposite formed by physically blending powders of aluminum oxide and silicon oxide.

It is desirable to use precursors of a higher purity to produce a nanoscale or submicron powder of a desired purity. For example, if a purity greater than x% (by metal weight basis) is desired, one or more precursors that are mixed and used may have purities greater than or equal to x% (by metal weight basis) to practice the teachings herein.

With continued reference to FIG. 1, the metal-containing precursor 100 (containing one or a mixture of metal-containing precursors) is fed into a high temperature process 106, which may be implemented using a high temperature reactor, for example. In some embodiments, a synthetic aid such as a reactive fluid 108 may be added along with the precursor 100 as it is being fed into the reactor 106. Examples

of such reactive fluids include, but are not limited to, hydrogen, ammonia, halides, carbon oxides, methane, oxygen gas, and air.

While the discussion herein teaches methods of preparing nanoscale and submicron powders of oxides, the teachings may be readily extended in an analogous manner to other compositions such as carbides, nitrides, borides, carbonitrides, and chalcogenides. These compositions can be prepared from micron-sized powder precursors of these compositions or by utilizing reactive fluids that provide the elements desired in these metal comprising compositions. In some embodiments, high temperature processing may be used. However, a moderate temperature processing or a low/cryogenic temperature processing may also be employed to produce nanoscale and submicron powders using the methods of the present invention.

The precursor 100 may be pre-processed in a number of other ways before any thermal treatment. For example, the pH may be adjusted to ensure precursor stability. Alternatively, selective solution chemistry, such as precipitation with or without the presence of surfactants or other synthesis aids, may be employed to form a sol or other state of matter. The precursor 100 may be pre-heated or partially combusted before the thermal treatment.

The precursor 100 may be injected axially, radially, tangentially, or at any other angle into the high temperature region 106. As stated above, the precursor 100 may be pre-mixed or diffusionally mixed with other reactants. The precursor 100 may be fed into the thermal processing reactor by a laminar, parabolic, turbulent, pulsating, sheared, or cyclonic flow pattern, or by any other flow pattern. In addition, one or more metal-containing precursors 100 can be injected from one or more ports in the reactor 106. The feed spray system may yield a feed pattern that envelops the heat source or, alternatively, the heat sources may envelop the feed, or alternatively, various combinations of this may be employed. In some embodiments, the spray is atomized and sprayed in a manner that enhances heat transfer efficiency, mass transfer efficiency, momentum transfer efficiency, and reaction efficiency. The reactor shape may be cylindrical, spherical, conical, or any other shape. Methods and equipment

such as those taught in U.S. Patent Nos. 5,788,738, 5,851,507, and 5,984,997 (each of which is specifically incorporated herein by reference) can be employed in practicing the methods of this invention.

In certain embodiments, the precursor feed conditions and feed equipment are engineered to favor flash boiling. Precursor may be fed utilizing any shape or size and device. Illustrative spray device include spray nozzle, tubular feed orifice, flat or bent nozzles, hollow pattern nozzle, flat or triangular or square pattern nozzle and such. In certain embodiments, a feed system that yields cavitation enhanced flash boiling is utilized for improved performance. In this regard, a useful guideline is to utilize a dimensionless number, commonly referred to as cavitation index (C.I.), which is defined, for purposes herein, as

$$\text{C.I.} = (P_o - P_v) / \rho V^2$$

where, P_o is the process pressure, P_v is the vapor pressure of the precursor in the feed nozzle, ρ is the density of the precursor, V is the average velocity of the precursor at the exit of the feed nozzle (volumetric feed rate divided by cross sectional area of the feed nozzle). In certain embodiments, a negative value of cavitation index defined above is favorable. In other embodiments, a value less than 15 for cavitation index is favorable. In yet other embodiments, a value less than 125 for cavitation index is favorable. In certain embodiments, the process pressure is maintained between 1 Torr and 10,000 Torr. In other embodiments, the process pressure is maintained between 5 Torr and 1,000 Torr. In certain embodiments, the process pressure is maintained between 10 Torr and 500 Torr. The process pressure can be maintained using any method such as, but not limited to, compressors, pressurized fluids, vacuum pumps, venturi-principle driven devices, such as eductors and the like.

If the density or the vapor pressure data for the precursor are unknown, it is recommended that they be measured by methods known in the art. Alternatively, as a useful guideline, higher feed velocities are favorable in certain embodiments. In certain embodiments, higher precursor feed temperatures are favorable. Higher feed temperature precursors are useful in certain embodiments wherein the precursor is

viscous or becomes viscous due to flow (viscosity is greater than that of water). In certain embodiments, it is useful to select achieve flash evaporation or cavitations of one or more components of the precursor stream upon spraying in the process reactor 106 (FIG. 1). This result may be achieved for example, by selecting suitable combinations of precursor formulations, solvents, feed spray equipment design (e.g.,
5 spray tip length, diameter, shape, surface roughness, etc.), and precursor feed parameters. In some embodiments, flash evaporation or cavitation can be achieved by engineering the fluid dynamics of the feed stream such that the vapor pressure P_v of the feed is a value close to or higher than process pressure. In some embodiments,
10 solvents may be added that increase vapor pressure of the feed. In other embodiments, the viscosity and wall friction may be used to increase the vapor pressure of the feed. In some embodiments, the temperature of the feed may be raised to increase the vapor pressure of the feed. In some embodiments, the process pressure may be reduced to achieve the C.I. index of less than zero.

15 With continued reference to FIG. 1, after the precursor 100 has been fed into reactor 106, it may be processed at high temperatures to form the product powder. In other embodiments, the thermal processing may be performed at lower temperatures to form the powder product. The thermal treatment may be done in a gas environment with the aim to produce products, such as powders, that have the desired porosity,
20 density, morphology, dispersion, surface area, and composition. This step produces by-products such as gases. To reduce costs, these gases may be recycled, mass/heat integrated, or used to prepare the pure gas stream desired by the process.

In embodiments using high temperature thermal processing, the high temperature processing may be conducted at step 106 (FIG. 1) at temperatures greater than 1500
25 K, in some embodiments greater than 2500 K, in some embodiments greater than 3000 K, and in some embodiments greater than 4000 K. Such temperatures may be achieved by various methods including, but not limited to, plasma processes, combustion in air, combustion in purified oxygen or oxygen rich gases, combustion with oxidants, pyrolysis, electrical arcing in an appropriate reactor, and combinations

thereof. Plasma can be used to provide reaction gases, or it can be used to provide a clean source of heat.

In certain embodiments, the high temperature is achieved by utilizing enriched oxygen, pure oxygen, or other oxidants. Adiabatic temperatures greater than 3000 K, 4000 K, or 5000 K can be achieved by utilizing purified oxygen. In certain
5 embodiments, a low cavitation index in combination with purified oxidant stream favors useful peak temperatures. In certain embodiments, a gas stream with greater than 25% oxygen is useful. In other embodiments, a gas stream with greater than 50% oxygen is useful. In other embodiments, a gas stream with greater than 75%
10 oxygen is useful. In yet other embodiments, a gas stream with greater than 95% oxygen is useful. In other embodiments, a gas stream with greater than 99.5% oxygen is useful. In certain embodiments, the reactor is operated at pressures greater than 500 Torr, greater than 1000 Torr, greater than 1500 Torr, or greater than 2000 Torr.

In some embodiments, the precursor and feed gas stream feed conditions are mixed in
15 a ratio that favors complete evaporation of the precursor. In certain embodiments, molar ratios of precursor to gas stream between 0.001 and 0.72 are useful. In certain embodiments, molar ratios of precursor to gas stream between 0.01 and 0.3 are useful. In certain embodiments, molar ratios of precursor and gas stream between 0.05 and 0.2 are useful for high temperature thermal processing. In certain embodiments, the
20 oxygen may be added in stages thereby controlling the thermokinetic ratio of fuel to oxidant. In other embodiments, the fuel to oxidant ratio may be maintained between the upper and lower flame limits for the precursor.

The combusted precursor and oxidant stream may be further heated utilizing various thermal sources such as, but not limited to, plasma processes (DC, RF, microwave,
25 transferred arc, non-transferred arc, etc.), radiation, nuclear energy, etc.

In certain embodiments, a plug flow system can be used. A plug flow eliminates axial mixing and thereby can yield narrow size distribution nanopowders. In certain embodiments, the design principle for the design of plug flow reactor system is given by

$$UL/D > \beta$$

Where,

U: axial velocity

L: axial length of the reactor

5 D: axial dispersion coefficient

β : plug flow index

In some embodiments, the plug flow index (β) can be 5 or more, in some embodiments 50 or more, and in some embodiments 500 or more. In some embodiments, the axial velocity of the process stream may be increased to achieve a high plug flow index. In other embodiments, the axial dispersion coefficient may be reduced. In some embodiments, the axial length of the reactor may be increased to achieve a high plug flow index.

A high temperature thermal process at 106 results in a vapor comprising elements, ionized species, and/or elemental clusters. After the thermal processing, this vapor is cooled at step 110 to nucleate nanopowders. The nanoscale particles form because of the thermokinetic conditions in the process. By engineering the process conditions, such as pressure, temperature, residence time, supersaturation and nucleation rates, gas velocity, flow rates, species concentrations, diluent addition, degree of mixing, momentum transfer, mass transfer, and heat transfer, the morphology of the nanoscale and submicron powders can be tailored. It is important to note that the focus of the process should be on producing a powder product that satisfies the end application specifics and customer needs.

The surface and bulk composition of the nanopowders can be modified by controlling the process temperature, pressure, diluents, reactant compositions, flow rate, addition of synthetic aids upstream or downstream of the nucleation zone, process equipment design and such. In certain embodiments, the nucleation temperature is adjusted to a temperature range wherein the condensed species is in liquid form at the process

pressure. In these cases, the nanomaterial product tends to take a spherical shape; thereafter the spherical nanomaterial is then cooled further to solidify. In certain embodiments, the nucleation temperature is adjusted to a temperature range wherein the condensed species is in solid form at the process pressure. In these embodiments, the nanomaterial product tends to take faceted shapes, platelet shapes, or a shape
5 wherein the particles' aspect ratios are greater than one. By adjusting the nucleation temperature in accordance with other process parameters, the shape, size and other characteristics of the nanomaterial can be varied.

In certain embodiments, the nanopowder comprising stream is quenched after cooling
10 to lower temperatures at step 116 to minimize and prevent agglomeration or grain growth. Suitable quenching methods include, but are not limited to, methods taught in U.S. Patent No. 5,788,738. In certain embodiments, sonic to supersonic processing before quenching and during quenching are useful. In certain embodiments, process stream velocities and quench velocities greater than 0.1 mach are useful (determined
15 at 298 K and 760 Torr or any other combination of temperature and pressure). In other embodiments, velocities greater than 0.5 mach can be used. In still other embodiments, velocities greater than 1 mach can be used. Joule-Thompson expansion based quenching can be used in certain embodiments. In other embodiments, coolant gases, water, solvents, cold surfaces, radiative cooling, convective cooling,
20 conductive cooling, cryogenic fluids and the like, either alone or a combination of such methods may be employed. In certain embodiments, quenching methods are employed which can prevent deposition of the powders on the conveying walls. These methods may include, but are not limited to, electrostatic means, blanketing with gases, the use of higher flow rates, mechanical means, chemical means,
25 electrochemical means, or sonication /vibration of the walls.

In some embodiments, the high temperature processing system includes instrumentation and software that can assist in the quality control of the process. Furthermore; in certain embodiments, the high temperature processing zone 106 is operated to produce fine powders 120, in certain embodiments submicron powders,
30 and in certain embodiments nanopowders. The gaseous products from the process

may be monitored for composition, temperature, and other variables to ensure quality at step 112 (FIG. 1). The gaseous products may be recycled to be used in process 108 or used as a valuable raw material when nanoscale and submicron powders 120 have been formed, or they may be treated to remove environmental pollutants if any.

5 Following quenching step 116, the nanoscale and submicron powders may be cooled further at step 118 and then harvested at step 120. The product nanoscale and submicron powders 120 may be harvested by any method. Suitable collection means include, but are not limited to, bag filtration, electrostatic separation, membrane filtration, cyclones, impact filtration, centrifugation, hydrocyclones, thermophoresis,

10 magnetic separation, and combinations thereof.

The quenching at step 116 may be modified to enable preparation of coatings. In such embodiments, a substrate may be provided (in batch or continuous mode) in the path of the quenching powder containing gas flow. By engineering the substrate temperature and the powder temperature, a coating comprising the submicron

15 powders and nanoscale powders can be formed.

In some embodiments, a coating, film, or component may also be prepared by dispersing the fine nanopowder and then applying various known methods, such as, but not limited to, electrophoretic deposition, magnetophoretic deposition, spin coating, dip coating, spraying, brushing, screen printing, ink-jet printing, toner

20 printing, and sintering. The nanopowders may be thermally treated or reacted to enhance their electrical, optical, photonic, catalytic, thermal, magnetic, structural, electronic, emission, processing, or forming properties before such a step.

It should be noted that the intermediate or product at any stage of the process described herein, or similar process based on modifications by those skilled in the art,

25 may be used directly as a feed precursor to produce nanoscale or fine powders by methods taught herein and other methods. Other suitable methods for producing nanoscale or fine powders include, but are not limited to, those taught in commonly owned U.S. Patent Nos. 5,788,738, 5,851,507, and 5,984,997, and co-pending U.S. Patent Application Nos. 09/638,977 and 60/310,967, which are all incorporated herein

30 by reference in their entirety. For example, a sol may be blended with a fuel and then

utilized as the feed precursor mixture for thermal processing above 2500 K to produce nanoscale simple or complex powders.

In summary, one embodiment for manufacturing powders consistent with teachings herein comprises (a) preparing a precursor comprising at least one metal; (b) feeding
5 the precursor under conditions wherein the cavitation index is less than 1.0 and wherein the precursor is fed into a high temperature reactor operating at temperatures greater than 1500 K, in certain embodiments greater than 2500 K, in certain
embodiments greater than 3000 K, and in certain embodiments greater than 4000 K; (c) wherein, in the high temperature reactor, the precursor converts into vapor
10 comprising the metal in a process stream with a velocity above 0.1 mach in an inert or reactive atmosphere; (d) cooling the vapor to nucleate submicron or nanoscale powders; (e) quenching the nucleated powders at high gas velocities to prevent agglomeration and growth; and (f) filtering the quenched powders from the gas suspension.

15 Another embodiment for manufacturing inorganic nanoscale powders comprises (a) preparing a fluid precursor comprising two or more metals, at least one of which is in a concentration greater than 100 ppm by weight; (b) feeding the said precursor into a high temperature reactor with a negative cavitation index (c) providing an oxidant such that the molar ratio of the precursor and oxidant is between 0.005 and 0.65 (d)
20 wherein the precursor and oxidant heat to a temperatures greater than 1500 K, in some embodiments greater than 2500 K, in some embodiments greater than 3000 K, and in some embodiments greater than 4000 K in an inert or reactive atmosphere; (e) wherein, in the said high temperature reactor, the said precursor converts into vapor comprising the metals; (f) cooling the vapor to nucleate submicron or nanoscale
25 powders (in some embodiments, at a temperature where the condensing species is a liquid; in other embodiments, at a temperature where the condensing species is a solid); (g) in some embodiments, providing additional time to let the nucleated particles grow to a desired size, shape and other characteristics; (h) quenching the nucleated powders by any technique to prevent agglomeration and growth; and (i)
30 processing the stream comprising quenched powder to separate solids from the gases.

In certain embodiments, the fluid precursor may include synthesis aids such as surfactants (also known as dispersants, capping agents, emulsifying agents, etc.) to control the morphology or to optimize the process economics and/or product performance.

- 5 One embodiment for manufacturing coatings comprises (a) preparing a fluid precursor comprising one or more metals; (b) feeding the said precursor at negative cavitation index into a high temperature reactor operating at temperatures greater than 1500 K, in some embodiments greater than 2500 K, in some embodiments greater than 3000 K, and in some embodiments greater than 4000 K in an inert or reactive atmosphere;
- 10 (c) wherein, in the high temperature reactor, the precursor converts into vapor comprising the metals; (d) cooling the vapor to nucleate submicron or nanoscale powders; (e) quenching the powders onto a substrate to form a coating on a surface to be coated.

The powders produced by teachings herein may be modified by post-processing, such as the processing taught by commonly owned U.S. Patent Application No. 10/113,315, which is hereby incorporated by reference in its entirety.

METHODS FOR INCORPORATING NANOPARTICLES INTO PRODUCTS

The submicron and nanoscale powders taught herein may be incorporated into a composite structure by any method. Some non-limiting exemplary methods are taught in commonly owned U.S. Patent No. 6,228,904, which is hereby incorporated by reference in its entirety.

The submicron and nanoscale powders taught herein may be incorporated into plastics by any method. In one embodiment, the method comprises (a) preparing nanoscale or submicron powders comprising metal(s) by any method, such as a method that employs fluid precursors and a peak processing temperature exceeding 1500 K; (b) providing powders of one or more plastics; (c) mixing the nanoscale or submicron powders with the powders of plastics; and (d) co-extruding or injection molding the mixed powders into a desired shape at temperatures greater than the softening

temperature of the powders of plastics but less than the degradation temperature of the powders of plastics. In another embodiment, a masterbatch of the plastic powder comprising nanoscale or submicron powders comprising metal(s) is prepared. These masterbatches can later be processed into useful products by techniques well known
5 to those skilled in the art. In yet another embodiment, the metal containing nanoscale or submicron powders are pretreated to coat the powder surface for ease in dispersability and to ensure homogeneity. In a further embodiment, injection molding of the mixed powders comprising nanoscale powders and plastic powders is employed to prepare useful products.

10 One embodiment for incorporating nanoscale or submicron powders into plastics comprises (a) preparing nanoscale or submicron powders comprising metal(s) by any method, such as a method that employs fluid precursors and peak processing temperature exceeding 1500 K; (b) providing a film of one or more plastics, wherein the film may be laminated, extruded, blown, cast, or molded; and (c) coating the
15 nanoscale or submicron powders on the film of plastic by techniques such as spin coating, dip coating, spray coating, ion beam coating, sputtering. In another embodiment, a nanostructured coating is formed directly on the film by techniques such as those taught in herein. In some embodiments, the grain size of the coating is less than 200 nm, in some embodiments less than 75 nm, and in some embodiments
20 less than 25 nm.

The submicron and nanoscale powders taught herein may be incorporated into glass by any method. In one embodiment, nanoparticles of metal(s) are incorporated into glass by (a) preparing nanoscale or submicron powders comprising metal(s) by any method, such as a method that employs fluid precursors and temperature exceeding
25 1500 K in an inert or reactive atmosphere; (b) providing glass powder or melt; (c) mixing the nanoscale or submicron powders with the glass powder or melt; and (d) processing the glass comprising nanoparticles into articles of desired shape and size.

The submicron and nanoscale powders taught herein may be incorporated into paper by any method. In one embodiment, the method comprises (a) preparing nanoscale or
30 submicron powders comprising metal(s); (b) providing paper pulp; (c) mixing the

nanoscale or submicron powders with the paper pulp; and (d) processing the mixed powders into paper by steps such as molding, couching, and calendering. In another embodiment, the metal containing nanoscale or submicron powders are pretreated to coat the powder surface for ease in dispersability and to ensure homogeneity. In a further embodiment, nanoparticles are applied directly on the manufactured paper or paper-based product; the small size of nanoparticles enables them to permeate through the paper fabric or reside on the surface of the paper and thereby functionalize the paper.

The submicron and nanoscale powders taught herein may be incorporated into leather, fibers, or fabric by any method. In one embodiment, the method comprises (a) preparing nanoscale or submicron powders comprising metal(s) by any method, such as a process that includes a step that operates above 1000 K; (b) providing leather, fibers, or fabric; (c) bonding the nanoscale or submicron powders with the leather, fibers, or fabric; and (d) processing the bonded leather, fibers, or fabric into a product. In yet another embodiment, the metal containing nanoscale or submicron powders are pretreated to coat or functionalize the powder surface for ease in bonding or dispersability or to ensure homogeneity. In a further embodiment, nanoparticles are applied directly on a manufactured product based on leather, fibers, or fabric; the small size of nanoparticles enables them to adhere to or permeate through the leather, fibers (polymer, wool, cotton, flax, animal-derived, agri-derived), or fabric and thereby functionalize the leather, fibers, or fabric.

The submicron and nanoscale powders taught herein may be incorporated into creams or inks by any method. In one embodiment, the method comprises (a) preparing nanoscale or submicron powders comprising metal(s), such as by the methods described herein that employs fluid precursors and peak processing temperature exceeding 1500 K; (b) providing a formulation of cream or ink; and (c) mixing the nanoscale or submicron powders with the cream or ink. In yet another embodiment, the metal(s) comprising nanoscale or submicron powders are pretreated to coat or functionalize the powder surface for ease in dispersability and to ensure homogeneity.

In a further embodiment, pre-existing formulation of a cream or ink is mixed with nanoscale or submicron powders to functionalize the cream or ink.

Nanoparticles comprising metal(s) may be difficult to disperse in water, solvents, plastics, rubber, glass, paper, etc. in certain cases. The dispersability of the nanoparticles can be enhanced in certain embodiments by treating the surface of the metal oxide powders or other metal comprising nanoparticles. For example, fatty acids (e.g. propionic acid, stearic acid and oils) or reactive organometallic compounds of silicon, titanium, or zirconium can be applied to or with the nanoparticles to enhance the surface compatibility. If the powder has an acidic surface, ammonia, quaternary salts, or ammonium salts can be applied to the surface to achieve desired surface pH. In other cases, acetic acid wash can be used to achieve the desired surface state. Trialkyl phosphates and phosphoric acid can be applied to reduce dusting and chemical activity. In yet other embodiments, the powder may be thermally treated to improve the dispersability of the powder.

Example 1: Aluminum Silicon Oxide Nanomaterials

OA[®] aluminum precursor from Chattem Chemicals was mixed with Octamethylcyclotetrasiloxane silicon precursor from Gelest Chemicals in a ratio that provided 44 atomic% Al and 56 atomic% Si. This mix was sprayed into a thermal plasma reactor described above at a rate of about 65 ml/min using about 180 standard liters per minute oxygen. The cavitation index for the feed was less than 125. The peak vapor temperature in the thermal plasma reactor, processed at velocities greater than 0.25 mach, was above 3000 K. The vapor was cooled and then quenched by Joule-Thompson expansion. The powders collected were analyzed using X-ray diffraction (Warren-Averbach analysis) and BET Surface Area Analyzer (Quantachrome). It was discovered that the powders were mostly amorphous (partly crystalline) and had a specific surface area of greater than 20 m²/gm. The refractive index of the powder was between 1.5 and 1.55.

Example 2: Aluminum Silicon Oxide Nanomaterials

OA[®] aluminum precursor from Chattem Chemicals was mixed with Octamethylcyclotetrasiloxane silicon precursor from Gelest Chemicals in a ratio that

provided 23 atomic% Al and 77 atomic% Si. This mix was sprayed into a thermal plasma reactor described above at a rate of about 65 ml/min using about 180 standard liters per minute oxygen. The cavitation index for the feed was less than 15. The peak vapor temperature in the thermal plasma reactor, processed at velocities greater than 0.5 mach, was above 3000 K. The vapor was cooled and then quenched by Joule-Thompson expansion. The powders collected were analyzed using X-ray diffraction (Warren-Averbach analysis) and BET Surface Area Analyzer (Quantachrome). It was discovered that the particles were mostly amorphous (partly crystalline) and had a specific surface area of greater than 40 m²/gm. The refractive index of the powder was between 1.47 and 1.51.

Example 3: Aluminum Silicon Oxide Nanomaterials

OAQ[®] aluminum precursor from Chattem Chemicals was mixed with Octamethylcyclotetrasiloxane silicon precursor from Gelest Chemicals in a ratio that provided 70 atomic% Al and 30 atomic% Si. This mix was sprayed into a thermal plasma reactor described above at a rate of about 65 ml/min using about 220 standard liters per minute oxygen. The cavitation index for the feed was less than 15. The peak vapor temperature in the thermal DC plasma reactor, processed at velocities greater than 0.5 mach, was above 3000 K. The vapor was cooled and then quenched by radiative cooling combined with expansion. The powders collected were analyzed using X-ray diffraction (Warren-Averbach analysis) and BET Surface Area Analyzer (Quantachrome). It was discovered that the powders were mostly amorphous (partly crystalline) and a specific surface area of greater than 30 m²/gm. The refractive index of the powder was between 1.57 and 1.64.

Example 4: Functionalized Aluminum Silicon Oxide Nanomaterials

100 grams of aluminum silicon oxide nanopowders from Example 1 were mixed with 12 grams of deionized water. To the mix, about 4 grams of isobutyltriethoxysilane dissolved in 10 grams of methanol was added. Next, the mix was heated to 110° C under dry argon for 30 minutes. While the gas was flowing, the powders were mixed. The powder was cooled and characterized. It was found that the powders were

hydrophobic and dispersed well in polymers and in non-polar solvents. The powders had been functionalized with isobutyl functional groups on the surface.

Example 5-6: Silver doped Aluminum Silicon Oxide Nanomaterials

10 grams of silane solution was prepared by mixing 5 grams of deionized water and 5
5 grams of N-(2-Amino ethyl)-3-Amino propyl trimethoxy silane. 25 grams of aluminum silicon oxide nanopowders from Example 1 were mixed with 10 grams of silane solution. Next, the mix was heated to 110° C under dry argon for 30 minutes. While the gas was flowing, the powders were mixed. The powder was cooled and characterized. Next the functionalized nanopowder was mixed into a solution
10 consisting of 2 wt% silver nitrate solution in water. The silver transferred from the solution to the N-(2-Amino ethyl)-3-Amino propyl functional groups on the surface of the powder. The powder was filtered and dried at 65° C in an oven. A white aluminum silicate nanopowder comprising silver was thus prepared. Such powders are useful in anti-microbial and other biocidal applications in form of clear coatings
15 and plastic composites.

In another example, instead of silver, the functionalized nanopowder was mixed into a solution consisting of 2 wt% copper nitrate solution in water. The copper ions transferred from the solution to the N-(2-Amino ethyl)-3-Amino propyl functional groups on the surface of the powder. The powder was filtered and dried at 65° C in
20 an oven. A purplish blue aluminum silicate nanopowder comprising of copper was thus prepared. Such powders are useful in anti-microbial and other biocidal applications in form of clear coatings and plastic composites. These examples show that the nanopowders can be surface functionalized and doped with positively charged species such as metal ions.

25 Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A method of manufacturing a nanomaterial composition of matter comprising
providing a precursor comprising one or more metals;
feeding the precursor in a reactor such that the cavitation index of the
5 fed precursor is less than 15;
processing, in the reactor, the precursor at a temperature greater than
1500 K to create a high temperature stream comprising the one or more metals from
the precursor;
nucleating a nanomaterial from the high temperature stream; and
10 quenching the nucleated nanomaterial.
2. The method of claim 1, wherein the cavitation index is negative.
3. The method of claim 1, wherein the processing temperature is greater
than 2500 K.
4. The method of claim 1, wherein the precursor is combined with an
15 oxidant prior to processing.
5. The method of claim 4, wherein the oxidant comprises oxygen.
6. A method of claim 4, wherein the molar ratio of the precursor to
oxidant is between 0.005 and 0.65.
7. The method of claim 1, wherein the precursor is a fluid.
- 20 8. The method of claim 1, wherein the reactor is operated at a pressure of
less than 1000 Torr.
9. The method of claim 1, wherein the processing temperature is greater
than 1000 K.
10. The method of claim 1, wherein the quenched nucleated nanomaterial
25 comprises particles having an aspect ratio greater than 1.

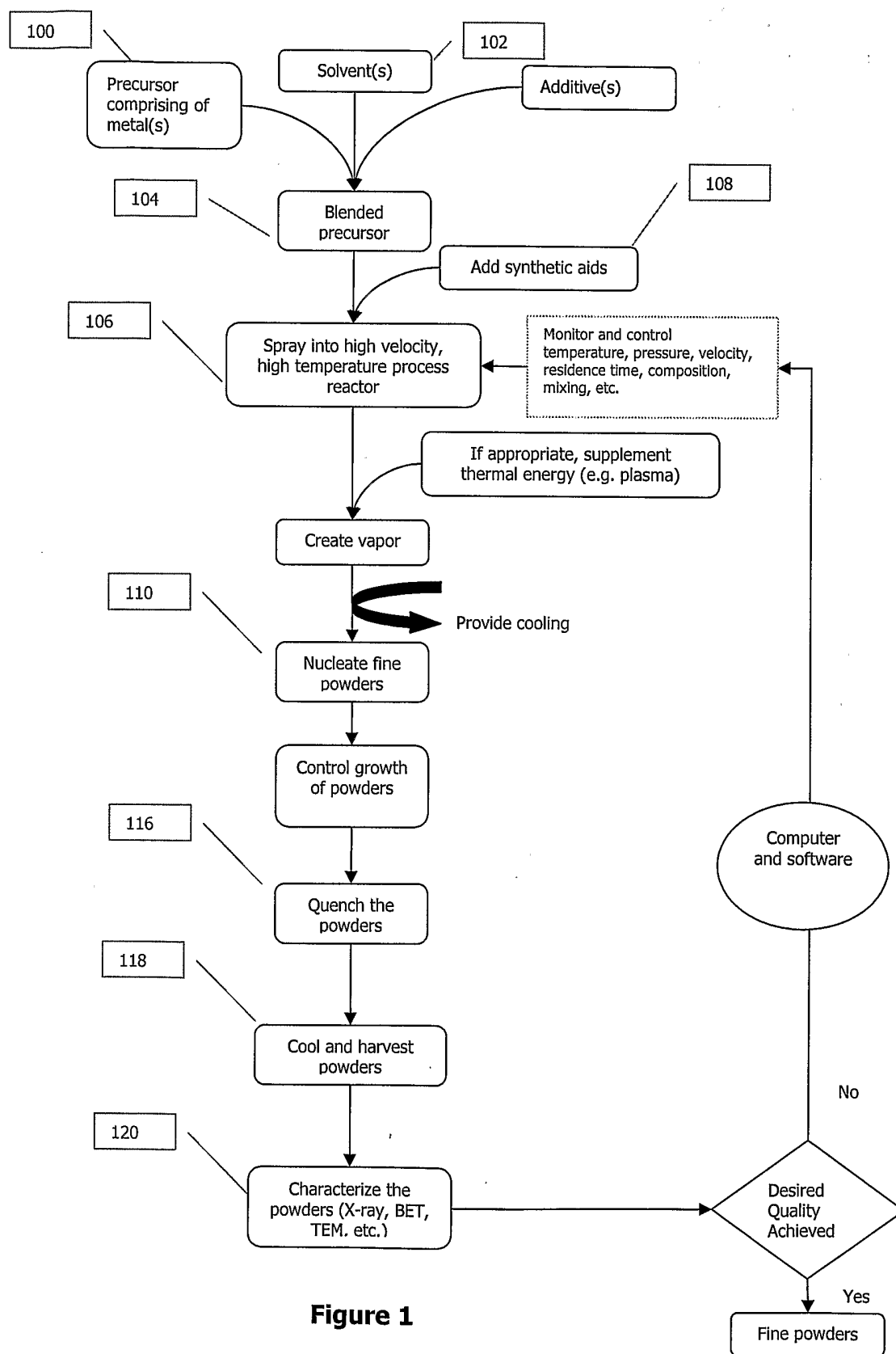
11. The method of claim 1, wherein the quenched nucleated nanomaterial comprises amorphous particles.

12. The method of claim 1, further comprising functionalizing the surface of the nanomaterial.

5 13. The method of claim 1, further comprising doping the nanomaterial with a metal ion.

14. The method of claim 13, wherein the metal ion is a silver or copper ion.

10 15. A product comprising the nanomaterial composition of matter produced using the method of claim 1.

**Figure 1**