POLYOL-BASED METHOD FOR PRODUCING ULTRA-FINE COPPER POWDERS

Inventors: Dan V. Goia, Potsdam, NY (US);
Daniel Andreescu, Potsdam, NY (US);
Brendan P. Farrell, Potsdam, NY (US)

Correspondence Address:
BROWN RAYSMAN MILLSTEIN FELDER & STEINER LLP
900 THIRD AVENUE
NEW YORK, NY 10022 (US)

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ABSTRACT
The present invention provides a metallic composition, which contains a plurality of ultra-fine metallic particles (e.g., ultra-fine copper, nickel, or silver particles) having at least one desirable feature, such as, tight size distribution, low degree of agglomeration, and high degree of crystallinity and oxidation resistance. The present invention further provides a method for forming the ultra-fine metallic particles. Also provided are a substrate or substrate coated with the ultra-fine metallic particles and a method of coating a substrate or substrate with the ultra-fine metallic particles. Furthermore, the present invention provides a method of controlling the size of ultra-fine metal particles formed in a reducing reaction in a liquid. Also provided is a method for producing ultra-fine metallic particles, which utilizes a concentrated reaction system.
Fig. 1
Fig. 2
Fig. 3
Fig. 5
POLYOL-BASED METHOD FOR PRODUCING ULTRA-FINE COPPER POWDERS

CROSS REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] The present invention relates generally to ultra-fine metallic compositions and methods of making thereof. The present invention further relates to methods of depositing ultra-fine metallic compositions onto various substrates.

BACKGROUND OF THE INVENTION

[0003] Ultra-fine metallic particles have many unique physical and chemical characteristics, which make them ideal materials for a variety of applications, such as electronics, catalysis, metallurgy, and decorative. Compared to the various particle-producing techniques used in the art, the methods based on the chemical precipitation in solutions provide several advantages, e.g., low manufacturing cost and a very good control of the mechanism of metal particles formation. Others in the art have successfully prepared micron and submicron-size metallic powders of Co, Cu, Ni, Pb, and Ag using chemical-based techniques, such as the ones based on the reduction in alcohols or polyols. For example, U.S. Pat. No. 4,539,041 discusses a method for producing micrometer-size metallic particles by using polyols to convert various metallic compounds into metal powders.

[0004] These procedures, however, are characterized by rather low concentrations of metallic precursors and consume large quantities of organic solvents per unit weight of metallic powder produced. Furthermore, the metallic powders produced using these procedures have a wide size distribution, a low degree of crystallinity, and in the case of the base metals, a pronounced tendency to oxidation.

SUMMARY OF THE INVENTION

[0005] The present invention provides a metallic composition, which includes a plurality of ultra-fine metallic particles (e.g., ultra-fine copper, nickel, or silver particles) having at least one desirable feature, such as tight size distribution, low degree of agglomeration, and high degree of crystallinity and oxidation resistance.

[0006] In one aspect, the present invention provides a method for forming compositions having a plurality of ultra-fine metallic particles (e.g., ultra-fine copper, nickel, or silver particles), and the metallic composition produced therewith, where the plurality of ultra-fine metallic particles may be obtained in accordance with a process that includes the steps of:

[0007] (a) forming a reaction mixture containing a precursor of a metal, a branched dispersing agent, and an alcoholic agent;

[0008] (b) adjusting the temperature of the reaction mixture to a temperature suitable for reducing the metal precursor to the metallic state ("the reaction temperature");

[0009] (c) maintaining the reaction mixture under the reaction temperature for a time sufficient to reduce the precursor of the metal to metal particles; and optionally,

[0010] (d) isolating the metal particles.

[0011] In one embodiment, the branched dispersing agent may be a branched polyol, e.g., pentaerythritol. In another embodiment, the reaction mixture further may contain at least one other dispersing agent, such as linear polyols (e.g., sorbitol and/or mannitol) and ammonium or sodium salts of polynaphthalene sulphonic/formaldehyde co-polymer. In yet another embodiment, the alcoholic agent may be 1,2-propylene glycol, 1,3-propylene glycol, diethylene glycol, or the combinations thereof. In still another embodiment, the method of the present invention may further include a step of adjusting the pH of the reaction mixture (e.g., by introducing a buffering agent, such as triethanolamine).

[0012] In another aspect, the present invention provides a substance or substrate coated with a plurality of ultra-fine metallic particles (e.g., ultra-fine copper, nickel, or silver particles) having at least one desirable feature, such as tight size distribution, low degree of agglomeration, and high degree of crystallinity and oxidation resistance.

[0013] Also provided is a method of coating a substance with a plurality of ultra-fine metallic particles (e.g., copper, nickel, or silver particles), and the coated substance produced therewith, including the steps of:

[0014] (a) forming a reaction mixture containing the substance, a precursor of a metal, a branched dispersing agent, and an alcoholic agent;

[0015] (b) adjusting the temperature of the reaction mixture to a temperature suitable for reducing the precursor of the metal to metal particles ("the reaction temperature");

[0016] (c) maintaining the reaction mixture under the reaction temperature for a time sufficient to reduce the precursor of the metal to metal particles and permit the resulting metal particles to form a coating on the surface of the substance; and optionally,

[0017] (d) isolating the coated substance.

[0018] In one embodiment, the branched dispersing agent may be a branched polyol, e.g., pentaerythritol. In another embodiment, the reaction mixture may further contain at least one other dispersing agent, such as linear polyols (e.g., sorbitol and/or mannitol) and ammonium or sodium salts of polynaphthalene sulphonic/formaldehyde co-polymer. In yet another embodiment, the alcoholic agent may be 1,2-propylene glycol, 1,3-propylene glycol, diethylene glycol, or the combinations thereof. In still another embodiment, the method of the present invention may further include a step of adjusting the pH of the reaction mixture (e.g., by introducing a buffering agent, such as triethanolamine).

[0019] In yet another aspect, the present invention provides a method of controlling the size of ultra-fine metal particles (e.g., copper, nickel, or silver particles) formed in a reducing reaction in a liquid, where the method includes the step of adjusting the pH of the liquid, e.g., by introducing a buffering agent into the liquid, such as triethanolamine. In one embodiment, the ultra-fine metal particles may be formed by reducing a precursor of the metal in the liquid containing a polyol composition. In another embodiment,
the polyol composition may contain a branched dispersing agent, such as a branched polyol (e.g., pentaerythritol). Further provided is a method for producing ultra-fine metallic particles, which utilizes a concentrated reaction system.

Additional aspects of the present invention will be apparent in view of the description that follows.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 includes images that depict the effects of buffering agent TEA on the copper particles produced by the method in accordance with one embodiment of the present invention, where the reaction mixture includes 50% 1,2-PG, 50-x % DEG, and x % TEA and (a) x=0; (b) x=1.5; (c) x=5; and (d) x=10. The images were acquired using field emission scanning electron microscope.

FIG. 2 shows the effects of buffering agent TEA on the size of the copper particles produced by the method according to one embodiment of the present invention.

FIG. 3 illustrates the effects of various mixtures of polyols on the size of the copper particles produced by the method according to one embodiment of the present invention, where the reaction mixture includes (a) 1,2-PG and TEA (90:10 v/v); (b) 1,2-PG, 1,3-PG, and TEA (50:40:10, v/v, respectively); and (c) 1,2-PG, DEG, and TEA (50:40:10, v/v, respectively). Images were acquired using a scanning electron microscope at two magnifications (5,000x and 10,000x).

FIG. 4 demonstrates the effects of changing the concentration of the copper salt on the size of the copper particles produced by the method according to one embodiment of the present invention, where the reaction mixture includes: (a) 0.174 g/cm³ CuCO₃; (b) 0.261 g/cm³ CuCO₃; (c) 0.348 g/cm³ CuCO₃; and (d) 0.400 g/cm³ CuCO₃. Images were acquired using a scanning electron microscope (5000x magnification).

FIG. 5 contains the typical XRD pattern of highly crystalline copper particles produced by the method according to one embodiment of the present invention, displaying a pronounced split of the (220), (311), and (222) reflections.

FIG. 6 shows the SEM images of nickel particles produced by the method according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As used herein and in the appended claims, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Thus, for example, reference to “a particle” includes a plurality of such particles, and reference to “the polyol” is a reference to one or more polyols and equivalents thereof known to those skilled in the art, and so forth. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety.

The present invention provides ultra-fine metallic particles having at least one desirable feature, such as, a tight size distribution, a high degree of crystallinity, oxidation resistance, and a low degree of agglomeration, or a combination thereof. The present invention also generally provides a more cost effective chemical based method for producing metallic powders than those known in the art. The present invention further generally provides a method for producing metallic powders having ultra-fine metallic particles of a particular size by reducing precursors of the metals in an alcoholic agent at higher concentrations than those used in the systems known in the art to produce particles with substantially the same sizes. The concentrated method or system of the present invention may therefore be used to reduce the cost of making ultra-fine metallic particles in terms of energy, resources, waste, etc.

In at least one embodiment of the invention, the present method or system beneficially produces metallic powders that include a plurality of ultra-fine metallic particles having at least one desirable feature, e.g., a tight size distribution, a high degree of crystallinity, oxidation resistance, and a low degree of agglomeration, or a combination thereof. As used herein and in the appended claims, the term “ultra-fine particles” generally includes particles having diameters of about 1 nm-10 µm, preferably, about 10-5,000 nm, and more preferably, 50-3,000 nm, and even more preferably, 100-1000 nm. The ultra-fine metallic particles may be the metallic particles of various metals, including, without limitation, transitional metals and noble metals, such as Ag, Au, Co, Cr, Cu, Fe, In, Ir, Mn, Mo, Ni, Nb, Os, Pd, Pt, Re, Rh, Ru, Sn, Ta, Ti, V, W, Zn, and the combinations thereof. In one embodiment, the metallic powders include a metal selected from the group consisting of Cu, Ni, and Ag.

Unlike other metallic powders appearing in the art, in one embodiment, the system of the present invention produces metallic powders that include ultra-fine metallic particles, particularly, isostructural ultra-fine metallic particles, that have a tight size distribution. The breadth of the size distribution, as used herein, generally refers to the degree of variation in the diameter of the ultra-fine metallic particles in a metallic composition. Tight, used in this context, indicates a relatively small variation in the size of the ultra-fine particles. In one embodiment, the ultra-fine metallic particles are deemed to have a tight size distribution when the diameters of at least about 85%, preferably, at least about 88%, and more preferably, at least about 95%, of the ultra-fine metallic particles of the present invention are within the range of Na=15% N, where N is the average diameters of the ultra-fine metallic particles. The diameters of the ultra-fine metallic particles may be measured by a number of techniques, such as, by an electron microscope, particularly, a scanning electron microscope (e.g., field emission scanning electron microscope).

The metallic powders produced with the system of the present invention may also include ultra-fine metallic particles that have a low degree of agglomeration. The degree of agglomeration may be expressed using the index of agglomeration $I_{aggl}$ which is the ratio between the average size distribution of the ultra-fine metallic particles ("PSD50%") and the average diameter of the particles. The average particle size distribution may be determined by any methods known in the art, including, but not limited to, dynamic light scattering (DLS), laser diffraction, and sedimentation methods, while the average particle size may be determined by averaging the diameter of the individual ultra-fine metallic particles obtained by, e.g., electron microscopy. An $I_{aggl}$ value of 1.0 indicates completely lack of agglomeration, while an increase in $I_{aggl}$ value indicates...
an increase in the degree of aggregation. In one embodiment, the powders of ultra-fine metallic particles of the present invention have a $d_{50}$ value of 1.2 or less.

The metallic powders produced in accordance with the present invention may also include ultra-fine metallic particles that have a high degree of crystallinity. The term “degree of crystallinity,” as used herein and in the appended claims, generally refers to the ratio between the size of the crystallites in the metallic powder and the diameter of the metallic particles. The size of the constituent crystallites may be deduced from XRD measurements using the Sherrer’s equation, while the particle size may be determined by electron microscopy. A larger ratio of the size of the crystallites in comparison to the diameter of the metallic particles indicates an increased degree of crystallinity and a lower internal grain boundary surface. In one embodiment, the ultra-fine metallic particles have a high degree of crystallinity if at least about 80%, preferably, at least about 85%, more preferably, at least about 90-95%, and even more preferably, about 100% of the ultra-fine metallic particles of the present invention are highly crystalline. The high degree of crystallinity is reflected by the visible splitting of the peaks corresponding to the (220), (311), and (222) reflections in the XRD spectrum (see, e.g. FIG. 5).

The metallic powders produced in accordance with the present invention may also include ultra-fine metallic particles that are resistant to oxidation. In one embodiment, the ultra-fine metallic particles of the present invention undergo minimal or insubstantial oxidation when exposed to the air in ambient environment for about 12 months or longer. Oxidation is generally minimal or insubstantial if the ultra-fine metallic particles display an increase of less than about 5-10% in their oxygen content as measured by the LECO combustion method. In another embodiment, the ultra-fine metallic particles of the present invention do not undergo substantial oxidation when exposed to a temperature of up to 100°C in ambient environment for about 120 minutes. In still another embodiment, the overall weight gain of the ultra-fine metallic particles is minimal or insubstantial when they are heated in the air at 20°C/min to about 200-220°C, and does not exceed about 80% of the theoretical weight gain when the temperature reaches about 800°C. For example, the theoretical weight gain of 100 g Cu particles when treated under the above condition is ~26 g. The weight gain of 100 g ultra-fine Cu particles of the present invention when treated under the same condition does not exceed ~21 g.

The present invention also provides methods for producing metallic powders, and also metallic powders produced therewith, that include a plurality of ultra-fine metallic particles that, in one embodiment, are obtained by:
(a) forming a reaction mixture containing a precursor of a metal, a branched dispersing agent, and an alcoholic agent;
(b) adjusting the temperature of the reaction mixture to a temperature suitable for reducing the precursor of the metal to metallic particles (“the reaction temperature”); (c) maintaining the reaction mixture under the reaction temperature for a time effective to reduce the precursor of the metal to metallic particles; and optionally, (d) isolating the metallic particles. In one embodiment, the method of the present invention further includes a step of adjusting the pH of the reaction mixture (e.g., by introducing a buffering agent, such as, triethanolamine).
The polyol composition used in the process of the present invention may be commanded by the particular reaction. A broad range of polyols may be used in the process, such as the polyols disclosed in U.S. Pat. Nos. 4,539,041 and 5,759,230, each of which is hereby incorporated herein by reference. The polyols may be either liquid or solid form. In one embodiment, 1,2-propylene glycol ("1,2-PG"), 1,3-propylene glycol ("1,3-PG"), diethylene glycol ("DEG"), or the combinations thereof, may be used in the reaction mixture. In another embodiment, a mixture of 1,2-PG and DEG may be used as the reducing polyol.

When forming the reaction mixture, the branched dispersing agent (e.g., the branched polyol) and the alcoholic agent may be either unheated or heated. Generally, the reaction temperature may be maintained or adjusted to about 80-350 C, or more preferably, about 110-200 C. For example, to produce ultra-fine Cu particles, 1,2-PG, DEG, and PE may be mixed and heated to bring the temperature of the mixture to about 70 C. The required amount of CuCO3 may then be added into the polyol mixture at about 80-850 C. After PE is fully dissolved, the reaction mixture may be further heated to bring the temperature of the mixture to an appropriate reaction temperature. In the present example, the reaction temperature is about 180-1850 C.

The resulting ultra-fine metal particles may be obtained following standard protocols known in the art, such as by precipitation, filtration, and centrifugation. The particles may further be washed, such as by using methanol or ethanol, and dried, such as by air, N2, or vacuum.

The size and the uniformity of the ultra-fine metallic particles may be affected by a variety of factors, such as the type of metal precursor, branched polyol, alcoholic agent, and dispersant used, the concentration of the metal ions, the reaction temperature, and the pH of the reaction mixture. In one embodiment, the pH of the reaction mixture may be adjusted to control the size of the ultra-fine metallic particles produced at any given metal precursor concentrations. The inventors discovered that pH changes significantly affect the reduction reaction and the formation of metallic particles. In a preferred embodiment, the pH of the reaction mixture may be adjusted by adding a buffering agent. The term “buffering agent” as used herein generally includes an agent which, upon addition to the reaction mixture, reduces the change of pH of the reaction mixture caused by the H+ produced during the reaction or when an acid or base is added into the reaction mixture. The buffering agent is added to the reaction mixture to control, e.g., increase, decrease, or stabilize, the pH of the reaction mixture in order to control the size of the particles produced by the reaction system at a given concentration of a metal precursor in the reaction mixture. In this respect, the pH of the reaction mixture may be controlled to produce smaller particles than would otherwise be possible at a particular concentration of the metal precursor. Examples of buffering agents are triethanolamine ("TEA"), 4-(2-hydroxyethyl)piperazin-1-ethanesulfonic acid ("HEPES"), 4-morpholinepropanesulfonic acid ("MOPS"), tris(hydroxymethyl)aminomethane ("Tris"), and N,N′-tris(hydroxymethyl)methyl]-2-aminoethanesulfonic acid ("TES"). In one embodiment, the buffering agent may be TEA.

The inventors discovered that the size of ultra-fine metallic particles formed by the process of the present invention may be significantly affected by the amount of buffering agent added to the reaction mixture. For example, in a typical reaction system with 1,2-PG (250 ml), DEG (250 ml), and CuCO3 (200 g), the pH of the reaction mixture measured at room temperature in the absence of PE decreases from about 8.6 at the beginning of the process to about 4.85 at the end of the reaction and the average size of the copper particles product is about 2.4 μm. The addition of 2% TEA (final concentration) raised the final pH to about 6.20 and the size of the copper decreased to about 1.5 μm. When 5% and 10% of TEA (final concentration) was introduced into the reaction mixture, the pH at the end of the reaction was about 7.70 and about 8.60, respectively, and the size of the copper particles produced by the process was reduced to about 700 nm and about 300 nm, respectively.

Moreover, controlling the pH of the reaction mixture during the reduction process offers additional unexpected benefits. For example, it may dramatically reduce the cost of making ultra-fine metallic particles by enabling the use of a concentrated reaction system. The polyol-based systems known in the art are rather diluted systems, i.e., the concentrations of the metal ions in these systems are kept low in order to form ultra-fine metal particles in the submicrometer scale, typically lower than 5-10%. Therefore, the diluted systems will consume more energy and materials (polyols, etc.) to produce a particular size of ultra-fine metallic particles than using a concentrated system. Furthermore, the concentrated system of the present invention reduces the cost of processing the organic solvent waste. In the polyol system of the present invention, the pH of the reaction mixture may be controlled, e.g., by the addition of a buffering agent, such as TEA. Thus, the reaction rate is not or significantly less affected by the potential change in the pH as a result of the presence of a large quantity of metal precursors in the system. For example, Cu particles with a size of about 300 nanometer may be produced by adding more than 200 g of CuCO3 into a reaction mixture of 500 ml (250 ml 1,2-PG, 200 ml DEG, and 50 ml TEA) following the process of the present invention, while Cu particles with a much larger size (about 2.4 μm) are formed when the same amount of CuCO3 is added into a reaction mixture where the pH is not controlled (250 ml 1,2-PG and 250 ml DEG).

The inventors also discovered that the types of polyol used in the process affect the size and uniformity of the metallic particles produced. For example, in a typical reaction, the ultra-fine copper particles formed in reaction mixture of 1,2-PG as the sole reducing polyol shown the widest particle size distribution (100-700 nm). The uniformity of the copper particles considerably improves when
polyol mixtures, such as a mixture of 1,2-PG and 1,3-PG or a mixture of 1,2-PG and DEG, are used (see, e.g., FIG. 3). Furthermore, comparing to the use of 1,3-PG, the use of DEG resulted in somewhat larger copper particles (e.g., 300 nm vs. 500 nm, respectively). The inventors further demonstrated that the copper particles produced by the process, which utilized a mixture of 1,2-PG and DEG, has the highest uniformity (i.e. the tightest size distribution) (see, e.g., FIG. 3).

The present invention further provides a substrate coated with a plurality of ultra-fine metallic particles, where the plurality of ultra-fine metallic particles have at least one desirable feature, such as, a tight size distribution, a low degree of agglomeration, a high degree of crystallinity, and oxidation resistance. The term “substrate” as used herein includes, without limitation, metallic subjects (e.g., metal particles, flakes, tubes, and sheets), plastic materials, ceramic subjects, fibers, films, glasses, polymers, organic materials (e.g., resins), inorganic materials (e.g., carbon nanotubes), and any other object capable of being coated with the ultra-fine metallic particles produced in accordance with the present invention. The ultra-fine metallic particles may be the metallic particles of various metals, preferably, Cu, Ni, and Ag.

In one aspect, the present invention provides a method of coating a substrate with a plurality of ultra-fine metallic particles, and also coated substrates produced therefrom, by: (a) forming a reaction mixture containing the substrate, a precursor of a metal, a branched dispersing agent (e.g., a branched polyol), and an alcoholic agent; (b) adjusting the temperature of the reaction mixture to a temperature suitable for reducing the precursor of the metal to metal particles (“the reaction temperature”); (c) maintaining the reaction mixture under the reaction temperature for a time effective to reduce the precursor of the metal to metal particles and permit the resulting metal particles to form a coating on the surface of the substrate; and optionally, (d) isolating the coated substance. In one embodiment, the ultra-fine metallic particles may be introduced to the surface of the substrate in such a manner that they form a uniform and continuous layer(s) the surface.

EXAMPLES

The following examples illustrate the present invention, which are set forth to aid in the understanding of the invention, and should not be construed to limit in any way the scope of the invention as defined in the claims which follow thereafter.

Example 1

Materials

The copper carbonate (CuCO₃) was supplied by Shepherd Chemical Co. 1,2-PG and DEG were obtained from Alfa Aesar (Ward Hill, Mass.). 1,3-PG and PE were obtained from Avocado Research Chemical Ltd., while TEA was purchased from Aldrich (Milwaukee, Wis.).

Example 2

Copper Particles Synthesis

All experiments were carried out in a 1 L, 4-necked round flask equipped with a Dean Stark trap and a refluxing condenser. The stirring was provided by a two inch Teflon—blade connected to a variable speed mixer. The amount of cupric carbonate used in the precipitation process was in general kept at 200 g (1.62 mol) although smaller or larger amounts were occasionally used as well (i.e., 87 g and 300 g). The CuCO₃ was added into 500 cm³ polyols or polyols mixture containing 15 g PE (for 200 g CuCO₃). The dispersant agent (PE) was initially added in polyols and heated at low power (10%) in the heating mantle to bring the temperature to 70° C. The required amounts of CuCO₃ were added into the flask at 80-85° C. after the PE was fully dissolved. The CuCO₃/polyol mixture was stirred at 500 RPM in all experiments. The mixture was then heated at 50% setting of heating power until the temperature reaches 180-185° C. The copper particles obtained were washed three times with ethanol (3x400 mL) and were filtered using a vacuum system and Whatmann #50 filter paper. The particles were then dried overnight at 80° C. in a regular oven.

Example 3

Particles Characterization

The morphology of copper particles was investigated by scanning electron microscopy (SEM) using a JEOL-JSM 6300 scanning microscope at 15 kV accelerating voltage and the magnification between 2500 and 10000. Also, the copper powders were analyzed by field emission scanning electron microscopy (FE-SEM) with 5 kV accelerating voltage and the same range of magnification using a JEOL JSM-7400F field emission scanning electron microscope.

Discussed below are results obtained by the inventors in connection with the experiments of Example 1-3:

In order to evaluate the effect of pH in the formation of Cu particles in polyols, variable amounts of triethanolamine (TEA) were added into the dispersion of CuCO₃ prior to the heating as shown in Table 1. The reaction time in the presence of TEA varied between 3 and 4 hours, the addition of more base tending to speed up the reaction. The images of copper particles produced in the manner described in the present invention, obtained by FE-SEM, are illustrated in FIG. 1.

Almost all copper particles prepared by the reduction of copper carbonate in polyols or mixtures of polyols in the presence of TEA are isometric and very crystalline in shape. Their diameter can be varied from several hundred nanometers (200-300 nm) to several micrometers (2-3 μm) by modifying the amount of TEA (pH) added into the reaction mixture.

The experimental conditions and data including the size range of the copper particles obtained at different pH values are summarized in Table 1. In all experiments containing TEA, the copper particles retained the original morphology obtained in the absence of TEA (pH=4.5).

The particles sizes shown in Table 1 were obtained by averaging the size of minimum 50 particles generated in each experiment.
### TABLE 1

<table>
<thead>
<tr>
<th>Polyol (ml)</th>
<th>TEA</th>
<th>CuCO₃</th>
<th>PE</th>
<th>Average particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-PG DEG</td>
<td>ml</td>
<td>(g)</td>
<td>(g)</td>
<td>pH²</td>
</tr>
<tr>
<td>500</td>
<td>0</td>
<td>0</td>
<td>200</td>
<td>15</td>
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<tr>
<td>250</td>
<td>250</td>
<td>0</td>
<td>0</td>
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<td>250</td>
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<td>250</td>
<td>200</td>
<td>50</td>
<td>50</td>
<td>200</td>
</tr>
</tbody>
</table>

¹ Letf:1018121.  
² The pH of emulsions was measured at room temperature at the end of the reaction.

[0056] The changes in the average diameter of copper particles size produced as a function of the concentration of TEA are illustrated in FIG. 2. The differences in average diameter of particles obtained in similar experimental conditions between different lots of CuCO₃ were ~10%.

[0057] In order to evaluate the influence of different polyol composition in the preparation of copper particles, several experiments were carried out using pure 1,2-PG and mixtures of 1,2-PG containing DEG and 1,3-PG respectively. In all these experiments a 10% content of TEA and the same amounts of PE (7 g) and CuCO₃ (87 g) were used. FIG. 3 a, b, c shows the SEM images at two magnifications (5000x and 10000x) of the copper particles formed in a 1,2-PG:DEG:TEA=50:40:10 (v/v) mixture and 1,2-PG:1,3-PG:TEA=50:40:10 (v/v), respectively. For comparison, FIG. 3 includes also the SEM of copper particles obtained in 1,2-PG:TEA=90:10 (v/v).

[0058] For copper particles formed in 1,2-PG/TEA mixture the SEM analysis shows the widest particle size distribution (100-700 nm). The uniformity of the copper particles improves when polyol mixtures were used. It appears that the nature of the second polyol affects the size of the particles, the addition of DEG generating larger particles (0.5 μm) than in the case of 1,3-PG (0.3 μm). Furthermore, the results of this set of experiments tend to suggest that the addition of DEG leads to the most uniform copper particles.

[0059] It has been shown in the inventors’ earlier work that, when the amount of the CuCO₃ is changed, the size of the copper particles decreases with the decrease in the concentration of the Cu ions of the system. This trend causes an increase in the cost of producing ultra-fine Cu particles with a decreased size. It is expected that, in more concentrated systems, the pH of the reaction mixture decreases more, causing a decrease in the reducing power of the polyol and a slowdown in the reaction rate of the second stage of the copper reduction (Cu²⁺→Cu⁰). The inventors demonstrated that the fine copper particles could be fact produced even in highly concentrated system providing that the pH of the reaction mixture is controlled. In order to evaluate the influence of CuCO₃ concentration on the copper particles size, a systematic study was carried out using 87 g (0.174 g/cm³); 174 g (0.348 g/cm³); 200 g (0.40 g/cm³) CuCO₃ in reduction process. For all experiments a fixed amount of PE (7 g) and a fixed 1,2-PG:DEG:TEA ratio (250:200:50, v/v) were used. The pH of the initial slurry did not change with the amount of carbonate used and it decreased only slightly during the reduction process. The SEM pictures at 5000x magnification of copper particles obtained at different CuCO₃ concentrations are illustrated in FIG. 4.

[0060] The average size copper particle was ~0.5 μm for all the CuCO₃ concentrations tested, the differences between separate precipitations being less than ±20%. A somehow better homogeneity was observed at the lowest concentration, probably because of the higher dipersant-metal ratio.

[0061] These results further confirm the hypothesis that the rate of the reduction with polyols is pH dependent and that by controlling the pH during the reaction the size of the resulting Cu particles can also be controlled. The discovery provided by the present invention may have significant implications in the production of ultra-fine Cu powders since it enables a manufacturing method which may be easily scaled up to produce ultra-fine Cu powder at very competitive prices.

[0062] Among the factors that may affect the size of copper particles produced by the chemical reduction of copper carbonate in polyols and/or polyols mixtures, one of the most influencing factor is the pH of solution. The inventors demonstrated that this parameter can be adjusted by adding TEA in controlled concentrations. At high pH values (8.6-9.0), such as when 10% TEA was added into the reaction mixture, smaller copper particles (size range 0.2-0.5 μm) are formed, while the sizes of copper particles increase with the decreasing of pH. The size of the copper particles is not substantially affected by the changes of pH when the value of the pH of the reaction mixture is less than 5.75 or higher than 8.5.

[0063] The second factor that influences the copper particle size is the composition of the polyol mixtures used in the precipitation process. When the copper powders were synthesized in only one polyol (e.g., 1,2-PG), a broad size distribution was obtained (1.5-2.6 μm). The uniformity of copper particles obtained in polyol mixtures is somehow improved compared to the case when pure 1,2-PG is used, the narrowest distribution being obtained in 1,2-PG:DEG mixtures (2-2.8 μm) (FIG. 3).

[0064] The third factor that influences the size of copper particles is the CuCO₃ concentration. When the pH of the system is not controlled, the diameters of the Cu particles varies significantly with the concentrations of the Cu precursor. However, when the pH is controlled by adding a buffering agent (i.e., TEA), the size of the copper particles was relatively stable for a wide range of CuCO₃ (0.174-0.40 g/cm³). An approximately 10% increasing in average diameter of copper particles obtained was observed in experiments using a higher CuCO₃ concentration (0.40 g/cm³) (FIG. 4).

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**Example 4**

**Preparation of Ultra-Fine Nickel Particles**

[0065] Nickel carbonate (NiCO₃) was supplied by Shepherd Chemical Co., 1,2-PG and DEG were obtained from Alfa Aesar (Ward Hill, Mass.). 1,3-PG and PE were obtained from Avocado Research Chemical Ltd., and the Palladium Chloride solution (PdCl₂) was obtained from OMG (South Plainfield, N.J.).
All experiments were carried out in a 1L 4-necked flask equipped with a refluxing condenser preceded by a dean stark trap and 7° extension. The stirring was provided by a two inch Teflon-flange connected to a variable speed mixer. The amount of nickel carbonate used in the precipitation process was in general kept at 140 g (1.18 mol). NiCO₃ was added into a 500 ml polyol mixture, composed of 50% PG and 50% DEG and 7 g PE. The dispersing agent, PE, was added in the polyol and heated at 75% power in the heating mantle for bringing the temperature up to 70° C. The required amount of NiCO₃ was then added into the flask at 80-85° C., after the PE was fully dissolved. The NiCO₃/polyol mixture was stirred at 500 RPM in all experiments. The mixture was continually heated at 75% power until the suspension reached the end point. The nickel particles shown in FIG. 6 were washed three times with ethanol (3x400 ml) and were filtered with a vacuum system using Whatman #50 filter paper. The particles were then dried overnight at 100° C. in a regular oven.

Example 5
Preparation of Ultra-Fine Silver Particles

All experiments were carried out in a 1L 4-necked flask equipped with a refluxing condenser preceded by a dean stark trap and 7° extension. The stirring was provided by a two inch Teflon-flange connected to a variable speed mixer. The amount of silver carbonate used in the precipitation process was in general kept at 100 g. Ag₂CO₃ was added into a 500 ml polyol mixture, composed of 50% PG and 50% DEG and 7 g PE. The dispersing agent was initially added in the polyol and mixed until completely dissolved. The required amount of Ag₂CO₃ was then added into the flask, after the PE was fully dissolved. The carbonate/polyol mixture was stirred at 500 RPM in all experiments. The mixture was continually heated until the suspension reached the end point.

While the foregoing invention has been described in some detail for purposes of clarity and understanding, it will be appreciated by one skilled in the art, from a reading of the disclosure, that various changes in form and detail can be made without departing from the true scope of the invention in the appended claims.

What is claimed is:

1. A metallic composition comprising a plurality of ultra-fine copper particles, wherein the plurality of ultra-fine copper particles is resistant to oxidation.

2. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles undergoes minimal oxidation for 12 months in ambient environment, wherein oxidation is minimal when the oxygen content of the ultra-fine copper particles is less than about 5-10% at the end of such period of time.

3. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles undergoes minimal oxidation when the plurality of ultra-fine copper particles is exposed to a temperature up to 100° C. for 120 minutes in air.

4. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles undergoes minimal oxidation when the plurality of ultra-fine copper particles is heated in air at 20° C./minute up to 200-220° C.

5. The metallic composition of claim 1, wherein oxidation is characterized by a weight gain in the plurality of ultra-fine copper particles and wherein the weight gain of the plurality of ultra-fine copper particles does not exceed about 80% of a theoretical weight gain for the plurality of ultra-fine copper particles when the plurality of ultra-fine copper particles is heated in air at 20° C./minute to 800° C.

6. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles has a tight size distribution.

7. The metallic composition of claim 6, wherein the plurality of ultra-fine copper particles has a tight size distribution when at least about 80% of the plurality of ultra-fine copper particles has a diameter within the range of Na±15% N, wherein N is an average diameter of the plurality of ultra-fine copper particles.

8. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles has a high degree of crystallinity.

9. The metallic composition of claim 8, wherein at least about 80-95% of the plurality of ultra-fine copper particle is highly crystalline.

10. The metallic composition of claim 1, wherein the plurality of ultra-fine copper particles has a low degree of agglomeration.

11. The metallic composition of claim 10, wherein the degree of agglomeration is measured with an L₅₀ value and wherein the L₅₀ of the plurality of ultra-fine copper particles is less than about 1.2.

12. A metallic composition comprising a plurality of ultra-fine copper particles, wherein the plurality of ultra-fine copper particles is obtained in accordance with the process comprising the steps of:
   (a) forming a reaction mixture comprising a precursor of copper, a branched dispersing agent, and an alcoholic agent;
   (b) adjusting the temperature of the reaction mixture to a reaction temperature suitable for reducing the precursor of copper to copper particles;
   (c) maintaining the reaction mixture under the reaction temperature for a time sufficient to reduce the precursor of copper to copper particles; and optionally,
   (d) isolating the copper particles.

13. The metallic composition of claim 12, wherein the branched dispersing agent is a branched polyol.

14. The metallic composition of claim 13, wherein the branched polyol is pentaerythritol.

15. The metallic composition of claim 12, wherein the reaction mixture further comprises at least one other dispersant selected from the group consisting of a linear polyol dispersant and a salt of polyvinylpyrrolidone sulphonate/formaldehyde co-polymer.

16. The metallic composition of claim 12, wherein the alcoholic agent is at least one polyol selected from the group consisting of 1,2-propylene glycol, 1,3-propylene glycol, and diethylene glycol.

17. The metallic composition of claim 16, wherein the alcoholic agent is the mixture of 1,2-propylene glycol and diethylene glycol.

18. The metallic composition of claim 12, wherein the precursor of copper is copper carbonate.
19. The metallic composition of claim 12, wherein the precursor of copper is a mixture of copper carbonate and at least one of copper acetate and copper salicylate.

20. The metallic composition of claim 12, wherein the reaction temperature is about 180-185°C.

21. The metallic composition of claim 12, wherein the process further comprises adjusting pH of the reaction mixture.

22. The metallic composition of claim 21, wherein pH of the reaction mixture is adjusted by introducing a buffering agent into the reaction mixture.

23. The metallic composition of claim 22, wherein the buffering agent is triethanolamine.

24. The metallic composition of claim 12, wherein the reaction mixture further comprises an agent which releases an organic counter ion.

25. The metallic composition of claim 24, wherein the organic counter ion is at least one of an acetate and a salicylate.

26. A method for forming a plurality of ultra-fine copper particles comprising the steps of:

(a) forming a reaction mixture comprising a precursor of copper, a branched dispersing agent, and an alcoholic agent;

(b) adjusting the temperature of the reaction mixture to a reaction temperature suitable for reducing the precursor of copper to copper particles;

(c) maintaining the reaction mixture under the reaction temperature for a time sufficient to reduce the precursor of copper to copper particles; and optionally,

(d) isolating the copper particles.

27. The method of claim 26, wherein the branched dispersing agent is a branched polyol.

28. The method of claim 27, wherein the branched polyol is pentaerythritol.

29. The method of claim 26, wherein the reaction mixture further comprises at least one other dispersant selected from the group consisting of a linear polyol dispersant and a salt of polynaphthalene sulphonyl/formaldehyde co-polymer.

30. The method of claim 26, wherein the alcoholic agent is at least one polyol selected from the group consisting of 1,2-propylene glycol, 1,3-propylene glycol, and diethylene glycol.

31. The method of claim 30, wherein the alcoholic agent is the mixture of 1,2-propylene glycol and diethylene glycol.

32. The method of claim 26, wherein the precursor of copper is copper carbonate.

33. The method of claim 26, wherein the precursor of copper is a mixture of copper carbonate and at least one of copper acetate and copper salicylate.

34. The method of claim 26, wherein the reaction temperature is about 180-185°C.

35. The method of claim 26, further comprising adjusting pH of the reaction mixture.

36. The method of claim 26, wherein the pH of the reaction mixture is adjusted by introducing a buffering agent into the reaction mixture.

37. The method of claim 36, wherein the buffering agent is triethanolamine.

38. The method of claim 26, wherein the reaction mixture further comprises an agent which releases an organic counter ion.

39. The method of claim 38, wherein the organic counter ion is at least one of an acetate and a salicylate.