

METHOD FOR THE PRODUCTION OF ULTRAFINE PARTICLES AND NANOCOMPOSITES

The present invention relates to methods for the production of ultrafine particles and nanocomposites. More particularly, the invention relates to methods using a combination
5 of chemical precipitation and mechanical milling to form the ultrafine particles or nanocomposites.

Ultrafine powders have significant potential for use in a wide range of applications including catalyst, magnetic recording media, magnetic fluids, optical materials and composite materials. Among the many physical and chemical methods available for the
10 preparation of ultrafine powders, precipitation is one which is widely used commercially as fine and ultrafine powders can be economically produced in large quantity by precipitation.

However, agglomeration is one of the major problems for precipitation. The precipitation process normally comprises two steps: precipitation and dehydration. Hydroxide
15 precursor is often the initial product after precipitation. Oxide particles have to be obtained after dehydration process, i.e. calcination at elevated temperatures. The particle size of oxide powder is strongly related to the size of agglomerates. Because agglomeration is always present to a certain degree in precipitated precursor, the quality of ultrafine particles is not easily controlled after the dehydration process. Particle size and
20 uniformity of particles characterize the quality of ultrafine powder.

High-energy mechanical milling (also known as mechanical alloying) has been used for production of fine powders with particle sizes typically in the range of from 0.2 to 2 μm .

Nanocomposite materials have been synthesized using mechanical alloying. The reduction of particles size and formation of nanocomposites are known as the results of fracture and
25 welding processes during mechanical milling.

Precursor after chemical precipitation normally consists of agglomerates formed by loosely connected amorphous hydroxide particles with particle sizes typically in the range of from

5 to 10 nm.

According to one aspect of the invention there is provided a method for the production of ultrafine particles, comprising the steps of:

- providing a precursor derived from a chemical precipitation process;
- 5 mechanically milling said precursor with a solid matrix such that said precursor is dispersed throughout said solid matrix;
- dehydrating said precursor during and/or after said mechanical milling step; and
- removing said solid matrix from a final mass comprising said solid matrix and said ultrafine particles to obtain said ultrafine particles.

10 According to another aspect of the invention, there is provided a method for the production of a nanocomposite consisting of ultrafine particles dispersed throughout a solid matrix, said method comprising the steps of:

- providing a precursor derived from a chemical precipitation process;
- mechanically milling said precursor with a solid matrix such that said precursor is
- 15 dispersed throughout said solid matrix; and
- dehydrating said precursor during and/or after said mechanical milling step.

There is also provided ultrafine particles and nanocomposites produced by either one of the immediately preceding two paragraphs respectively.

The bonds between hydroxide particles are preferably easily broken by mechanical fracture

20 during mechanical milling. As such, the precursors are preferably dried at relatively low temperatures prior to milling to avoid hard agglomerations. The collision energy of mechanical milling is advantageously high enough to be effective in the fracture of agglomerates. The products after mechanical milling comprise a final mass of precursor particles, for example metal hydroxide particles or hydroxide agglomerates of

25 coprecipitated metal hydroxides such as iron hydroxide, zinc hydroxide, zirconia hydroxide, aluminum hydroxide, barium hydroxide and agglomerates thereof, embedded in the solid matrix.

The final mass of precursor and matrix is preferably calcined at elevated temperature for dehydration. In the case of a metal hydroxide precursor, ultrafine oxide particles will therefore be dispersed in the matrix material. The calcination temperature and reaction time may be determined according to the particular precursor being used. However, the
5 calcination is preferably carried out at a temperature of from about 200°C to about 1200°C, preferably for a period of from about 1 to about 2 hours.

As will be recognised from the above discussion the method may also be used for the synthesis of compounds or phases, particularly if they can not be formed directly after dehydration process and calcination at a higher temperature is required, e.g., $\text{BaFe}_{12}\text{O}_{19}$
10 and $\alpha\text{-Al}_2\text{O}_3$. A suitable matrix which will not react with the compound or phase during the calcination process should be chosen. The matrix will, in accordance with the method, be removed afterward.

Many metals can be produced by hydrogen or carbon monoxide reduction of oxides at temperatures which are not significantly higher than the temperatures required for
15 dehydration. The method of the invention may also be used for the fabrication of ultrafine metallic powders via hydrogen or carbon dioxide reduction of the as-milled mixture and subsequent removal of matrix material. For example, ultrafine iron or nickel particles can be obtained by calcination of the mixture of iron or nickel oxide in the solid matrix at temperatures from 400-500°C under hydrogen atmosphere.

20 The matrix material can be removed by washing with water or acid, if it is soluble in water or acid. The matrix material may also be removed by evaporation, if it has low melting temperature or high vapor pressure at not very high temperatures. Preferably the matrix material is NaCl, and is removed by washing of the final mass.

If the matrix material is not to be removed, the final product is a nanocomposite consisting
25 of ultrafine particles, for example metal oxide or metal particles, in the solid matrix. Therefore, nanocomposite materials can be fabricated by the invented technique in accordance with the second mentioned aspect of the invention described above.

The various features and embodiments described above in relation to the first mentioned aspect of the invention will still apply to this aspect of the invention. However, as the solid matrix is not to be removed from the final mass by washing or otherwise, the solid matrix may be, for example SiO_2 .

- 5 As discussed above, this technique can be used for production of a wide variety of ultrafine powders including oxide ceramics and metals. The high-energy mechanical mill may be of any suitable known type, for example, vibrated ball mill, planetary ball mill and attritor which is described in U.S. Patent No 2,764,359. The high-energy mechanical milling is termed as mechanical milling at a high energy level. The typical processing

10 parameters are listed as follows:

Collision energy	0.1 - 1.0 Joule
Ball/powder mass ratio:	2:1 - 50:1
Milling time:	Typically less than 48 hours
Atmosphere:	Air or inert gas, for example argon or nitrogen

- 15 The following examples are provided for exemplification only and should not be construed as limiting on the claims in any way.

Example 1 - Synthesis of Ultrafine Iron Oxide Particles

The starting materials include: ferric nitrate of reagent grade ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, purity > 99%, Fisher Scientific), an ammonium hydroxide solution (28%-30% NH_3 , Ajax Chemicals, Australia) and sodium chloride (purity > 99.5%, Merck, Germany). Iron hydroxide suspension was prepared by dissolving an appropriate amount of ferric nitrate in deionized water, followed by adding a desirable amount of ammonium hydroxide solution. The hydroxide precursor was retrieved from the solution by filtration, repeatedly washed with deionized water, and dried at a low temperature in a freeze drier. A mixture of the as-dried hydroxide precursor and sodium chloride (weight ratio: 1:4) was loaded and sealed in a hardened steel vial with steel balls (5 mm in diameter) under air atmosphere. The weight ratio of the balls to the powder was 12:1. The mechanical ball milling was carried out in a Spex 8000 mixer/mill for up to 20 hours. The as-milled powder was calcined at 600 °C for

1 hour, washed with deionized water for several times and dried at 100 °C in an oven to deliver ultrafine α -Fe₂O₃ powder.

Fig.1 shows the X-ray diffraction patterns of the hydroxide precursor, the as-milled powder, and the calcined and washed powder. No crystallized iron hydroxide phase can be detected from the x-ray diffraction pattern of the hydroxide precursor. The as-milled powder consisted of a mixture of sodium chloride and α -Fe₂O₃. The formation of α -Fe₂O₃ is due to the dehydration and crystallization of hydroxide precursor during milling. Post-milling calcination was conducted to improve the crystallinity of α -Fe₂O₃. A high purity α -Fe₂O₃ phase was obtained after the calcination at 600°C for 1 hour and subsequent washing process, as no other phase detected in the powder by XRD phase analysis.

The dehydration and crystallization of hydroxide during the ball milling process can also be confirmed from the results of differential scanning calorimetry (DSC) analysis. Fig. 2 shows the DSC curve for the hydroxide precursor heated from room temperature to 600°C in N₂ with the heating rate of 10 °C/min. Two strong and broad peaks can be observed. The evaporation of the absorbed water results in the first peak at about 140 °C with the on-set temperature of 100°C and the further dehydration and crystallization from iron hydroxide to α -Fe₂O₃ cause another peak at about 360°C. However for the DSC curve of the as-milled powder, there is only one broad peak at about 100°C, as shown in Fig. 3. Because the dehydration and crystallization had happened during the high energy milling process, no peak at about 360 °C can be observed for the as-milled powder.

The TEM micrograph of the precipitation-derived precursor is shown in Fig. 4. The morphology of the precursor is irregular hydroxide agglomerates with a wide distribution of agglomeration sizes. Fig. 5 shows the TEM micrograph of the as-milled powder after the removal of sodium chloride. The powder can be well-dispersed in deionized water and uniform particles with a mean size of less than 10 nm can be observed from the TEM micrograph. After the as-milled powder was calcined at 600°C for 1 hour followed by the removal of sodium chloride, well-crystallized α -Fe₂O₃ ultrafine powder can be obtained. The calcined α -Fe₂O₃ powder did not exhibit a higher degree of particle agglomeration than that of the as-milled powder. Most of the synthesized particles had a size of ~10 nm (Fig.

6.), which is not much bigger than that of the as-milled powder. For many precursor-derived ceramic powders, a calcination at an intermediate temperature often results in an increase in particle size and in the degree of particle agglomeration. However, by comparing Fig. 5 and Fig. 6., no such changes were observed between the calcined α -Fe₂O₃ powder and the as-milled one. This is believed to be due to the existence of sodium chloride, which served as a dispersant during the calcining process.

If the hydroxide precursor was calcined at 600°C for 1 hour without milling, α -Fe₂O₃ with the particle size ranging from 50-150 nm was formed, as shown in Fig. 7. This particle size is five to fifteen times bigger than that of the α -Fe₂O₃ prepared by ball milling followed by calcination. The existence of an inert matrix in the milling process is necessary for the preparation of ultrafine α -Fe₂O₃ powder by the present method.

The iron hydroxide precursor was mechanically milled without adding sodium chloride. The iron hydroxide can be reduced to α -Fe₂O₃ during the mechanical milling. Particles with the size ranging from 10-20 nm exhibit high degree agglomeration and form irregular agglomerates, as shown in Fig. 8. All of these results show that, for the preparation of ultrafine α -Fe₂O₃ particles by the present process, it is necessary to mill the hydroxide precursor under the presence of sodium chloride.

In order to study the effect of collision energy on morphology of ultrafine Fe₂O₃ particles, steel balls of 20 mm in diameter were used for mechanical milling. A similar result was obtained in comparison with the result using 5 mm diameter balls. In addition, an iron hydroxide powder after drying at room temperature was used as the starting material. The Ultrafine Fe₂O₃ powder obtained using this hydroxide precursor was not different with the ultrafine powder obtained using freeze dried hydroxide precursor as the starting material.

Ultrafine α -Fe₂O₃ particles have also been successfully prepared using an planetary mill, where the particle size was similar to that prepared using a Spex 8000 mixer/mill. Larger quantity of ultrafine powder of up to 50 g was produced using a Fritch 5 Planetary Mill. This result has shown that large quantity production is possible to be realized by this technique, if large-scaled mechanical mills can be used.

Example 2 - Synthesis of Ultrafine Barium Ferrite Particles

The starting materials include: barium nitrate and ferric nitrate of reagent grade ($\text{Ba}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, purity >99%, Fisher Scientific), an ammonium hydroxide solution (28.0-30.0% NH_3 , Ajax Chemicals, Australia), sodium chloride (purity > 99.5%, Merck, Germany), and deionized water. $\text{Ba}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in deionized water at the Ba/Fe ratio of 1:7 to prepare a homogeneous solution. An appropriate amount of ammonia solution was added drop-wise into the solution while it was stirred. This resulted in the formation of coprecipitated Ba-Fe-hydroxides. The hydroxide precursor was retrieved from the solution by filtration, followed by washing using deionized water and dried at a low temperature in a freeze drier. Using a Spex 8000 mixer/mill, the as-dried precursor was milled with sodium chloride and 5mm steel balls in a hardened steel vial under air atmosphere for 20 hours. The as-milled powder was calcined at 600, 700 and 800 °C for 2 hours and washed with deionized water to remove sodium chloride.

Fig.9 shows the XRD patterns for the Ba-Fe hydroxide precipitate and the powder calcined at 700, 800 °C followed by washing process, respectively. For the Ba-Fe hydroxide precursor, no crystallized phase can be detect from the XRD pattern. For the powder calcined at 700 °C for 2 hours and followed by the removal of sodium chloride, only the peaks of crystallized $\text{BaFe}_{12}\text{O}_{19}$ can be observed. The crystallinity of $\text{BaFe}_{12}\text{O}_{19}$ is further enhanced when the calcination temperature is raised to 800 °C.

Fig. 10 is a bright field TEM micrograph showing the coprecipitation-derived precursor from the composition with an initial Ba/Fe ratio of 1:7. It consists of non-uniform hydroxide agglomerates. After milled with NaCl for 20 hours, the hydroxide agglomerates were separated into nano-sized particles with some degrees of particle agglomeration. There is a dramatic change in particle morphology when the as-milled powder is calcined at 800 °C for 2 hours, as illustrated in Fig. 12. The calcined barium ferrite powder exhibits a hexagonal particle morphology and is well dispersed, The average size of the calcined barium ferrite particles is in the range of 50-100 nm.

The magnetic properties of the calcined barium ferrite powders were measured at room

temperature using a VSM. as the calcination temperature is raised from 700 to 800 °C, there is an increase in saturation magnetization from 58.7 emu/g to 67.8 emu/g and an enhancement in intrinsic coercivity from 5.21kOe to 5.49kOe. The observed improvement in magnetic properties is believed to be due to the enhancement in crystallinity of barium ferrite particles.

Example 3 - Synthesis of Ultrafine Zinc Oxide Particles

ZnO ultrafine particles were synthesized by milling the precipitated zinc hydroxide with sodium chloride. Details of the process are described in Example 1. The resulting particle sizes were in the range of 10-20 nm, as determined from transmission electron microscopy measurement. Fig. 12 shows the typical morphology of nano ZnO particles produced by the present technology.

Example 4 - Synthesis of Ultrafine Zirconia Oxide Particles

ZrO₂ particles were synthesized by milling the precipitated zirconia hydroxide with sodium chloride. Details of the process are described in Example 1. The resulting particle sizes were in the range of 50-100 nm, as determined from transmission electron microscopy measurement.

Example 5 - Synthesis of Ultrafine β - and α -Al₂O₃ Particles

β - and α -Al₂O₃ particles were synthesized by milling the precipitated aluminum hydroxide with sodium chloride and subsequent calcination. Details of the process are described in Example 1. Ultrafine β -Al₂O₃ particles were obtained after dehydration at 600°C and washing process. The particle sizes were in the range of 10-20 nm according to our TEM study. The as-milled powders were calcined at 1200°C and α -Al₂O₃ powder can be collected after the removal of sodium chloride matrix. The resulting particle sizes were in the range of 100-200 nm, as determined from transmission electron microscopy measurement.

Example 6 - Synthesis of Fe_2O_3 - SiO_2 Composite

Fe_2O_3 - SiO_2 nanocomposite was synthesized by milling precipitated iron hydroxide with SiO_2 using a Spex 8000 Mixer/Mill. The XRD pattern showed that the as-milled powder consists two different phases: α - Fe_2O_3 and SiO_2 . The resulting sub-micron powder contained nano-
5 scaled α - Fe_2O_3 particles embedded in SiO_2 matrix.

It will be understood that the invention will also be useful in preparing other composites such as Fe_3O_4 - SiO_2 , Fe-SiO_2 , Fe_2O_3 - Al_2O_3 etc.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be
10 understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.



CLAIMS

- 1 1. A method for the production of ultrafine particles, comprising the steps of:
2 providing a precursor derived from a chemical precipitation process;
3 mechanically milling said precursor with a solid matrix such that said
4 precursor is dispersed throughout said solid matrix;
5 dehydrating said precursor during and/or after said mechanical milling step;
6 and
7 removing said solid matrix from a final mass comprising said solid matrix
8 and said ultrafine particles to obtain said ultrafine particles.
- 1 2. A method according to claim 1, wherein said precursor is dried at low
2 temperature prior to said mechanical milling step.
- 1 3. A method according to claim 1, wherein said precursor is a metal hydroxide
2 or an hydroxide agglomerate of coprecipitated metal hydroxides.
- 1 4. A method according to claim 3, wherein said metal hydroxide or hydroxide
2 agglomerate is selected from the group consisting of iron hydroxide, zinc hydroxide,
3 zirconia hydroxide, aluminum hydroxide, barium hydroxide and agglomerates thereof.
- 1 5. A method according to claim 3, comprising, after said milling step, calcining
2 the milled precursor and solid matrix at elevated temperature to form a dispersion of metal
3 oxide particles throughout said solid matrix.
- 1 6. A method according to claim 5, wherein said calcination is carried out at a
2 temperature of from about 200°C to about 1200°C.
- 1 7. A method according to claim 1, wherein said precursor is a metal hydroxide,
2 and said method comprises the steps of:
3 prior to said removal of said solid matrix, calcining the milled precursor
4 and solid matrix at elevated temperature to form a dispersion of metal oxide particles



5 throughout said solid matrix; and
6 reducing said metal oxide particles by hydrogen or carbon monoxide
7 reduction.

1 8. A method according to claim 7, wherein said reduction comprises calcination
2 of said metal oxide particles and said solid matrix at a temperature of from above 200°C
3 under hydrogen or carbon monoxide atmosphere.

1 9. A method according to claim 1, wherein said solid matrix is water or acid
2 soluble, and said removal step comprises washing said final mass with water or acid.

1 10. A method according to claim 9, wherein said solid matrix is NaCl.

1 11. A method according to claim 1, wherein said mechanical milling step is
2 carried out in a high-energy mill selected from a vibrated ball mill, planetary ball mill and
3 attritor.

1 12. A method according to claim 1, wherein said mechanical milling step is
2 carried out for a period of less than about 48 hours.

1 13. A method for the production of a nanocomposite consisting of ultrafine
2 particles dispersed throughout a solid matrix, said method comprising the steps of:
3 providing a precursor derived from a chemical precipitation process;
4 mechanically milling said precursor with a solid matrix such that said
5 precursor is dispersed throughout said solid matrix; and
6 dehydrating said precursor during and/or after said mechanical milling step.

1 14. A method according to claim 13, wherein said precursor is dried at low
2 temperature prior to said mechanical milling step.

1 15. A method according to claim 1, wherein said precursor is a metal hydroxide.



1 16. A method according to claim 15, wherein said metal hydroxide is iron
2 hydroxide.

1 17. A method according to claim 15, comprising, after said milling step, calcining
2 the milled precursor and solid matrix at elevated temperature to form a dispersion of metal
3 oxide particles throughout said solid matrix.

1 18. A method according to claim 17, wherein said calcination is carried out at a
2 temperature of about 200°C for a period of about 1 hour.

1 19. A method according to claim 17, further comprising reducing said metal
2 oxide particles by hydrogen or carbon monoxide reduction.

1 20. A method according to claim 19, wherein said reduction comprises
2 calcination of said metal oxide particles and said solid matrix at a temperature of above
3 200° under hydrogen or carbon monoxide atmosphere.

1 21. A method according to claim 13, wherein said solid matrix is SiO₂.

1 22. A method according to claim 13, wherein said mechanical milling step is
2 carried out in a high-energy mill selected from a vibrated ball mill, planetary ball mill and
3 attritor.

1 23. A method according to claim 13, wherein said mechanical milling step is
2 carried out for a period of less than about 48 hours.

1 24. Ultrafine particles when produced by a method according to any one of
2 claims 1 to 12.



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- 1 25. Ultrafine particles according to claim 24, selected from the group consisting
2 of α - Fe_2O_3 , ZnO , ZrO_2 , α - and β - Al_2O_3 , and $\text{BaFe}_{12}\text{O}_{19}$.
- 1 26. A nanocomposite when produced by a method according to any one of claims
2 13 to 23.
- 1 27. A nanocomposite according to claim 26, consisting of Fe_2O_3 - SiO_2 composite
2 Fe_3O_4 - SiO_2 composite, Fe-SiO_2 composite, or Fe_2O_3 - Al_2O_3 composite.