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Synthesis of Tetragonal Phase Stabilized Nano and Submicron Sized Nanoparticles.

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SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES

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OTHER PUBLICATIONS


(Continued)

ABSTRACT

Novel, monodispersed, spherical ZrO₂ particles in the size range of approximately 10 to approximately 600 nm exhibiting metastable tetragonal crystal structure at room temperature and novel methods of preparation. The ZrO₂ particles are approximately 100% in the tetragonal phase at room temperature and can be pure and free of foreign oxides. The novel method can include mixing zirconium-alkoxide and an alcohol, forming preparation one, followed by separately dissolving completely de-ionized water and a polymeric steric stabilizer in an alcohol forming preparation two. Next the preparations can be mixed with vigorous stirring while subjecting the materials to hydrolysis and condensation reactions with very slow stirring. Next, there is waiting for the formation of a sol from the mixture, followed by drying at approximately 80 degrees C. to form resultant material followed by crushing the resultant material.

7 Claims, 7 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
Fig. 2 (a)

Fig. 2 (b)
Figure 3

As Synthesized

200 °C

600 °C

400 °C

2-θ [°]

10 20 30 40 50 60 70 80
Figure 4

As Synthesized

800 °C

600 °C

400 °C
Figure 5

图例：

- (111)ₜ
- 600 °C
- 400 °C

图表显示了在不同温度下的2-θ角度分布。
SYNTHESIS OF TETRAGONAL PHASE STABILIZED NANO AND SUBMICRON SIZED NANOPARTICLES

This invention claims the benefit of priority from U.S. Provisional application No. 60/408,325 filed Sep. 5, 2002, and was supported in part by National Science Foundation (NSF) Grant # EEC:0136710.

FIELD OF INVENTION

This invention relates to nanoparticles and more particular to monodispersed, spherical ZrO₂ particles in the size range of approximately 10 to approximately 600 nm, exhibiting metastable tetragonal crystal structure at room temperature and this invention provides the synthesis, for the first time, using the sol-gel technique and without doping any trivalent impurities, of monodispersed, spherical ZrO₂ particles in the size range of approximately 10 to approximately 600 nm, exhibiting metastable tetragonal crystal structure at room temperature. This invention has revealed using high-resolution transmission electron microscopy that “hard-aggregates” forming tendency of ZrO₂ nanocrystallites of size approximately 30 to approximately 45 nm is responsible for stabilizing the high-temperature metastable tetragonal phase, at room temperature within large sized (500-600) nm undoped ZrO₂ particles.

BACKGROUND AND PRIOR ART


This type of transformation can take place near the crack tip due to local stress concentration, which can blunt the crack tip as a result of the development of compressive stresses associated with the phase transformation; thus, delaying the crack propagation and resisting subsequent fracture.

Zirconia is used as a dispersed phase in oxide (alumina) (Kosmac, T., Swain, M. V. Claussen, N. Mater. Sci. Eng. 1984, 71, 57), as well as non-oxide (carbides, borides, and nitrides) (Swain, M. V. Mater. Forum 1988, 11, 182.) ceramics to increase their fracture toughness, strength, and hardness. This stress induced transformation has also been shown to increase the plasticity from the shape deformation and accommodation strains, which are associated with the transformation. (Middle, B. C. Kelly, P. M. Mater Forum 1988, 11, 182.) Increase in the wear and corrosion resistance of nanostructured ceramic coatings as a result of stress-induced phase transformation has also been reported. (Aita, C. R., In Advances in Cating: TMS Annual Meeting, Warrendale, Pa., 1995 p. 235) Besides this, tetragonal ZrO₂ also finds application as catalyst/catalyst support for various gas-phase reactions. (Haruta, M. Kobayashi, T., Sano, H., Yamada, N Chem Lett. 1987, 829, 405 and Knell, A. Barnickel, P. Baiker, A. Wokaum, A. J. Catal. 1992, 137, 506.) Hence, synthesizing ZrO₂ particles with metastable tetragonal crystal structure is important.

Doping zirconia with trivalent impurities has been a traditional approach for the metastable tetragonal phase stabilization. (Ping, L., Chen, L. W., Penner-Hahn, J. E., J. Am Ceram Soc. 1994, 77, 188.) Particle size has also been observed to have its own effect on the metastable tetragonal phase stability in nanocrystalline zirconia. (Garvie, R. C., J. Phys. Chem 1965, 69, 1238, and Nitsche, R, Rodewald, M, Skandan, G, Guess, H., Hahn, H. Nanostruct. Mater. 1996, 7, 535, and Nitsche, R, Wintener, M, Hahn, H, Nanostruct. Mater. 1995, 6, 1979). Due to the existence of a critical nanoparticle size for the metastable tetragonal phase stabilization, the tetragonal phase stabilization within the submicron sized ZrO₂ particles has been unachievable.

SUMMARY OF THE INVENTION

The first objective of this invention is to provide ultra fine approximately 10 to approximately 600 nm and more particularly approximately 10 to approximately 30 nm and sub-micron sized (approximately 500 to approximately 600 nm) ZrO₂ nanoparticles that are in the metastable tetragonal phase.

The second objective of this invention is to provide a method for synthesizing particles of the size range of approximately 10 to approximately 600 nm and more particularly nano (approximately 10 to approximately 30 nm) and sub micron (approximately 500 to approximately 600 nm) ZrO₂ nanoparticles in the metastable tetragonal phase.

The third objective is to provide coatings of ZrO₂ coatings on metal substrates.

A preferred embodiment of the invention includes monodispersed, spherical zirconia (ZrO₂) particles of approximately 10 to approximately 600 nm, which exhibit metastable tetragonal crystal structure at room temperature. The ZrO₂ particles are approximately 100% in the tetragonal phase at room temperature, and the particles are pure and free of foreign oxides.

A preferred method for the synthesis of monodispersed, spherical ZrO₂ particles, which exhibit approximately 100% metastable tetragonal structure at room temperature, of sizes of approximately 10 to approximately 600 nm, in powder form can include various steps. The initial step can include mixing zirconium-alkoxide and an alcohol, forming preparation one, followed by separately dissolving completely de-ionized water and a polymeric steric stabilizer in an alcohol forming preparation two. Next the preparation one and the preparation two can be mixed with vigorous stirring for a approximately few minutes only, subjecting the materials to hydrolysis and condensation reactions with very slow stirring. Next, there is waiting for the formation of a sol from the mixture. Next, there is drying at approximately 80 degrees C to form resultant material followed by crushing the resultant material.

The polymeric steric stabilizer can be an organic polymer containing —OH or ether group. The polymeric steric stabilizer can be from one of the group consisting of hydroxypropyl cellulose polymer (HPC), polyvinylalcohol, ethylene glycol, and hexamethyldisilazane. The zirconium-alkoxide can be zirconium (IV) n propoxide and the alcohol can be anhydrous alcohol. Synthesis can take place under normal atmospheric conditions. The polymeric steric stabilizer can be an HPC polymer, and have a molecular weight of approximately 80,000 to approximately 1,000,000.

Further objects and advantages of this invention will be apparent from the following detailed description of the presently preferred embodiments which are illustrated schematically in the accompanying drawings.
BRIEF DESCRIPTION OF THE FIGURES

FIG. 1a shows nanocrystalline (approximately 20 to approximately 25 nm) sized spherical ZrO₂ particles synthesized using the sol-gel technique under the processing conditions of R=60 and HPC=1.0 g/L.

FIG. 1b shows monodispersed, submicron sized approximately 500 to approximately 600 nm spherical ZrO₂ particles synthesized using the sol-gel technique under processing conditions of R=5 and HPC=1.0 g/L after calcinations at 400 degrees C for 2 hours.

FIG. 2a shows HRTEM analysis of monodispersed submicron sized spherical ZrO₂ particles synthesized under the processing conditions of R=5 and HPC=1.0 g/L after calcinations at 400 degrees C for 2 hours.

FIG. 2b shows the SAED patterns obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm) spherical ZrO₂ particles at the center of a particle after calcination at 400 degrees C for 2 hours.

FIG. 2c shows SAED patterns obtained for monodispersed submicron sized (approximately 500 to approximately 600 nm) spherical ZrO₂ particles at the edge of a particle after calcination at 400 degrees C for 2 hours.

FIG. 3 shows typical broad scan XRD patterns, within 20 range of 10 degrees to 80 degrees, obtained for nanocrystalline ZrO₂ particles of size approximately 20 to approximately 25 nm after calcinations at 400 degrees C for 2 hours, synthesized under the processing conditions of R=60, and HPC=1.0 g/L.

FIG. 4 shows typical broad scan XRD patterns, within 20 range of approximately 10° to approximately 80°, obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm) spherical ZrO₂ particles, after calcination at 400° C for 2 h, synthesized under the processing conditions of R=5 and HPC=1.0 g/L.

FIG. 5 shows typical narrow scan XRD patterns obtained for monodispersed, submicron sized (approximately 500 to approximately 600 nm) spherical ZrO₂ particles, after calcination at higher temperatures for 2 h, synthesized under the processing conditions of R=5, and HPC=1.0 g/L.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Before explaining the disclosed embodiments of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangements shown since the invention is capable of other embodiments. Also, the terminology used herein is for the purpose of description and not of limitation.

This invention demonstrates for the first time that, at room temperature, the stability of the metastable tetragonal phase within the submicron sized ZrO₂ particles strongly depends on the aggregation tendency of ZrO₂ nanocrystallites. As a result of strong aggregation of ZrO₂ nanocrystallites, the inventors have been able to synthesize both nano (approximately 10 to approximately 30 nm) and large sized (approximately 500 to approximately 600 nm) ZrO₂ particles having 100% tetragonal crystal structure. This particle size is much larger than the critical size of approximately 6 nm, reported in the prior art, for the stabilization of 100% tetragonal phase.

To prepare the nanoparticles of the invention, pure zirconium (IV) n-propoxide anhydrous ethanol (approximately 200 proof) and the HPC polymer (hydroxypyrrolylcellulose, molecular weight approximately 50,000 g/mol) were used as a polymeric steric stabilizer were obtained from Aldrich Co and used as received.

Other alcohols and zirconium alkoxides may also be used. Other polymeric steric stabilizers may also be used such as any compound with —OH or other groups, for example polyvinylalcohol, ethylene glycol, or hexamethyldisilazane.

Other ceramic oxides can be used in addition to zirconium, for example, tin, indium, and titanium. Nanocrystalline ZrO₂ powder is synthesized by hydrolysis of zirconium (IV) n-propoxide in an alcohol solution. The beakers used in the experiments were cleaned, washed with deionizer water, dried completely and rinsed with anhydrous 200 proof ethanol. During synthesis, two different but equal parts of alcohol solutions were prepared. In the first part, deionized water was dissolved into anhydrous 200 proof ethanol using two different R values (R=5 and 60), which is the ratio of molar concentration of water to zirconium (IV) n-propoxide. HPC polymer (HPC)=1.0 g/L was then added to this part and was dissolved completely by stirring the solution overnight using a magnetic stirrer. The second part of the alcohol solution was then prepared by completely dissolving zirconium (IV) n-propoxide (0.1 M) in anhydrous 200 proof ethanol under normal atmospheric conditions and homogenized using magnetic stirring for a few minutes only. After preparing each solution, both the beakers were sealed immediately with paraffin tape.

Hydrolysis of zirconium (IV) n-propoxide was then carried out under atmospheric conditions by rapidly mixing the two sealed solutions under vigorous stirring. The formation of ZrO₂ particles was evident from the white color of the resulting sol due to immediate precipitation.

The sol was stirred very slowly for approximately 4 hours and then held under static conditions for 24 h to ensure completion of the hydrolysis and condensation reactions. The sol was subsequently dried at approximately 80° C. using Petri dishes in order to remove the solvent completely.

The small gel pieces obtained were then crushed to obtain the nanocrystalline ZrO₂ powder, which was calcined at different temperatures ranging from approximately 400° to approximately 800° C in air for the phase evolution study. The samples were heated at a rate of approximately 30° C/min up to the calcination temperature, held at that temperature for 2 hours, and then slowly cooled to room temperature in the furnace. The as-synthesized nanocrystalline ZrO₂ powders were then examined using a Phillips EM400 transmission electron microscope (TEM) at 120 kV.

A high-resolution field TEM (HRTEM) (FEI-Philips Tecnai F30) was used to observe lattice images showing different orientations of nanocrystals within a submicron sized ZrO₂ particle, after calcination at approximately 400° C for 2 h. Bright field TEM images at 300 kV were taken to observe the lattice. Selected-area electron diffraction (SAED) patterns were taken to analyze the crystal structure. SAED patterns collected near the edge and from the center of the particle, provided the presence of nanocrystals within a submicron sized particle.
monoclinic phase is observed for the tetragonal phase, after calcinations at approximately 400°C. The temperature of metastable tetragonal polymorph of ZrO<sub>2</sub> is stabilized at room temperature within the monodispersed submicron sized (approximately 500 to approximately 600 nm) spherical ZrO<sub>2</sub> particles without doping any trivalent impurity. Various theories have been proposed for the stabilization of metastable tetragonal phase in nanocrystalline ZrO<sub>2</sub> at room temperature.

Garvie, R. C. J Phy. chem, 1965, 69, 1238) experimentally (using XRD) and using thermodynamic calculations, showed the existence of a critical size of 20 nm, below which the metastable tetragonal phase is stable in nanocrystalline ZrO<sub>2</sub> and above which the monoclinic phase is stable. Mitsubishi et al. (J. Am. Ceram. Soc. 1974, 57, 97) however, showed that the metastable tetragonal phase can be stabilized in ZrO<sub>2</sub> nanocrystallites of size greater than approximately 30 nm due to the strain energy involved at the interphase boundaries resulting from the simultaneous presence of monoclinic and tetragonal phases within the crystallites. By HRTEM analysis Nitsche et al further showed that the metastable tetragonal phase can be stabilized in ZrO<sub>2</sub> nanocrystallites of size greater than approximately 30 nm due to the strain energy involved at the interphase boundaries resulting from the simultaneous presence of monoclinic and tetragonal phases within the crystallites. By HRTEM analysis Nitsche et al further showed that the metastable tetragonal phase can be stabilized in ZrO<sub>2</sub> nanocrystallites of size greater than approximately 30 nm due to the strain energy involved at the interphase boundaries resulting from the simultaneous presence of monoclinic and tetragonal phases within the crystallites. 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the appearance of tetragonal as well as monoclinic phases when these ZrO₂ nanocrystallites are calcined at the crystallization temperature of 400 degrees C. With increased calcinations temperature above 400 degrees C., the phase transformation possibly proceeds in a manner as described schematically in FIG. 6c.

The tetragonal-to-monoclinic phase transformation in ZrO₂ is athermal in nature. As a result, a specific amount of monoclinic phase is formed at each calcination temperature, as observed in FIG. 3. As mentioned earlier, monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles are composed of small nanocrystallites of size approximately 45 nm after calcination at 400°C. The nanocrystallite size of approximately 45 nm is also larger than the predicted and observed critical size of approximately 30 nm 10 and approximately 6 nm 11, 12 respectively for approximately 100% metastable tetragonal phase stabilization. However, interestingly, no monoclinic phase formation is observed after crystallization of submicron sized ZrO₂ particles at 400°C. FIG. 4.

Moreover, the nanocrystallites within the submicron sized ZrO₂ particles are observed to grow due to calcination at 600°C, which is indicated by the decrease in the FWHM of the (111) peak with increase in the calcination temperature. Even after the growth of the nanocrystallites above approximately 45 nm size, no tetragonal to monoclinic phase transformation is observed at approximately 600°C. Hence, the tetragonal-to-monoclinic phase transformation appears to be suppressed with the submicron sized ZrO₂ particles at 600°C. Thus, the phase evolution behavior exhibited by the monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles is in contrast with that of ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm.

It is noted that ZrO₂ nanocrystallites (approximately 45 nm) form hard-aggregates of size approximately 500 to approximately 600 nm, under the processing conditions of R 5, (HPC) 1.0 g/L while ZrO₂ nanocrystallites of size approximately 20 to approximately 25 nm, synthesized under the processing conditions of R 60, (HPC) 1.0 g/L, form loose-agglomerates. It appears that due to the formation of hard-aggregates, the tetragonal-to-monoclinic phase transformation, which is accompanied by volume expansion, is suppressed at approximately 400°C and approximately 600°C. As a result, monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles having metastable tetragonal crystal structure are successfully synthesized in the present investigation.

The stabilization of metastable of tetragonal phase via proposed mechanism, which involves the suppression of volume increase associated with the tetragonal-to-monoclinic phase transformation, due to dense agglomeration of nanocrystallites within monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles, is supported by the following observations: First, the volume expansion associated with the tetragonal to monoclinic phase transformation would cause many stresses and strains to be included in the structure that might lead to fracture of the particles. However, no such type of fracture of monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles has been observed, which supports the stabilization of tetragonal phase in the large sized particles. Second, there is substantial evidence (obtained via HRTEM) of little or no free volume in the monodispersed, submicron sized (approximately 500 to approximately 600 nm), spherical ZrO₂ particles. Analogous to the glass transition in polymers, if there were free volume in these large particles, this excess free volume would permit the phase transition to take place. Finally, considering the precursors involved during the sol gel synthesis of ZrO₂ particles, there is no evidence of any group III impurity that might be otherwise stabilizing the tetragonal phase.

Nanosized (approximately 20 to approximately 25 nm) and submicron sized (approximately 500 to approximately 600 nm), monodispersed, spherical ZrO₂ particles are successfully synthesized using the sol-gel technique. The tendency of ZrO₂ nanocrystallites (approximately 45 nm) to form hard-aggregates is observed to be responsible for the high-temperature metastable tetragonal phase stabilization, at room temperature, within the submicron sized ZrO₂ particles.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:

1. Monodispersed, spherical zirconia (ZrO₂) particles of approximately 10 to approximately 600 nm, pure and free of foreign oxides exhibiting metastable tetragonal crystal structure at room temperature are produced by a sol-gel process comprising the steps of:
   a) mixing zirconium-alkoxide and an alcohol, forming preparation one;
   b) separating completely-de-ionized water and a polymeric steric stabilizer in an alcohol forming preparation two;
   c) mixing the preparation one and the preparation two for approximately a few minutes while subjecting the mixture to hydrolysis and condensation reactions with very slow stirring;
   d) waiting for the formation of a sol from the mixture;
   e) drying at approximately 80 degrees C. to form resultant material;
   f) crushing the resultant material; and
   g) forming spherical zirconia (ZrO₂) particles with 100% tetragonal crystal structure having aggregation and loose agglomeration properties.
2. The ZrO₂ particles as in claim 1, wherein said particles are approximately 10 to approximately 30 nm.
3. The ZrO₂ particles as in claim 1, wherein said particles are approximately 500 to approximately 600 nm.
4. A coating of monodispersed, spherical ZrO₂ particles of claim 1 on a metal substrate, wherein said particles are approximately 10 to approximately 600 nm in size, are synthesized using a sol-gel technique, are pure and free of foreign oxides, exhibit metastable tetragonal crystal structure and are 100% in the tetragonal phase.
5. The coating, as in claim 4, wherein said particles are approximately 10 to approximately 30 nm in size.
6. The coating, as in claim 4, wherein said particles are approximately 500 to approximately 600 nm in size.
7. A nanocrystalline ZrO₂ powder formed from monodispersed, spherical ZrO₂ particles of claim 1 wherein the resultant material is small gel pieces that are crushed to obtain the nanocrystalline ZrO₂ powder.

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