

Description

This invention relates to sol-gel derived fine microstructured ceramic oxide/non-oxide and non-oxide ceramic microbubbles. In another aspect, the invention relates to a process for preparing such microbubbles. The microbubbles are useful as abrasives, in low density structural composites, as fillers, catalyst substrates, machinable refractories, and as controlled release drug carriers.

Use of ceramics in fiber form and in composites is well known. Ceramics, especially in solid spherical form, useful as catalyst supports, catalysts, reflective materials, and abrasives, are also well known. In recent years, many ceramics have been made using the sol-gel process.

The sol-gel process is well known in the art - see for example United States Patent Nos. 4,349,456, 3,709,706, and 4,290,847. A general reference on modern technology is A. Westwood et al., "High Technology Ceramics", Cutting Edge Technologies, National Academy of Engineering, National Academy Press, Washington, D.C. (1984) pages 117 to 130.

Preparation of hollow, ceramic microspheres by spray drying is taught in U. S. Patent No. 4,421,562. A shortcoming of this technique is that the spheres suffer from holes and cracks.

U. S. Patent No. 4,637,990 describes hollow, ceramic, porous microspheres prepared by a blowing technique. The resultant ceramic microspheres have diameters of 2000 to 4000 micrometers; smaller size bubbles are not taught.

U. S. Patent No. 4,279,632 discloses a method and apparatus for producing concentric hollow spheres by a vibration technique on extruded materials to break up the material into individual, spherical bodies. This method is useful with low melting point material such as glass or metal which is fluid at elevated operating temperatures.

Non-vitreous ceramic metal oxide microcapsules and a process for making such microcapsules from sol-gel precursors is described in U.S. Patent No. 4,349,456. The gel bubbles produced by this method are filled with organic dehydrating liquid which must be removed with considerable care to prevent fracture of the bubbles.

Hollow ceramic balls prepared by a combination of coating, sintering, and reduction are disclosed in U. S. Patent No. 4,039,480; however, the process is complex, and the balls so obtained are large (e.g., 5 by 7 mesh size which is 2.79 to 3.96 millimeters).

Ceramic metal oxide microspheres prepared by impregnating hollow, organic resin microspheres with a metal compound, and firing to remove adjuvants is disclosed in U. S. Patent No. 3,792,136. The resultant hollow microspheres generally have large diameters of 50 micrometers to 10 millimeters (mm) and in one example, when the average diameter was 3mm, the wall thickness is disclosed to be 17 micrometers.

U. S. Patent No. 2,978,340 describes inorganic microspheres prepared from a fusion (melt or vitreous) process using a gassing agent. The product is not uniform in size, and the microspheres are not all hollow.

U. S. Patent No. 3,975,194 teaches hollow microballoons prepared by an involved process. The resultant balloons have a non-uniform cross-section.

U. S. Patent No. 4,772,511 discloses using vegetable oils or derivatives thereof as forming media for the preparation of zirconia based ceramic beads.

The present invention provides free-flowing, discrete ceramic microbubbles consisting essentially of either 1) a non-oxide ceramic component and an oxide ceramic component, or 2) non-oxide ceramic, each microbubble having a fine microstructured ceramic wall and a single central cavity, said microbubbles having a diameter in the range of 1 to 300 micrometers and a wall thickness of less than 10 percent of the diameter of the microbubbles. Preferably the microbubbles have wall thicknesses of 0.5 to about 8 percent of the diameter of the bubbles. Microbubbles of the invention can be essentially all non-oxide ceramic or they can be a combination of oxide ceramic and non-oxide ceramic. The oxide component may be present in a solid solution with the non-oxide component, or the two components may be in admixture with each other as separate phases identifiable by X-ray diffraction analysis (XRD). Particularly useful bubbles have a composition of non-oxide to oxide components in the range of 95:5 to 5:95 parts by weight. These ratios may be determined by X-ray diffraction analysis. Bubbles of this invention may consist essentially of all non-oxide phases or they may be made up of a mixture with at least one of the nitride, carbide and oxide phases. Especially useful are bubbles which are essentially 100 weight percent non-oxide containing; although those containing less than 5 weight percent oxide are also useful.

In another aspect the present invention provides shaped ceramic articles containing ceramic microbubbles in accordance with the invention.

In a further aspect, this invention provides a method for providing green microbubbles comprising the steps of:

a) adding a mixture comprising of sol precursor and a volatile liquid bloating agent to a bubble promoting medium at a temperature in the range from 50 to 150 °C to provide green, hollow, microbubbles, said sol precursor comprising either

- i) a non-oxide ceramic component precursor and an oxide ceramic precursor component, or
- ii) a non-oxide ceramic component precursor,

said bloating agent having a boiling point below the temperature of said bubble promoting medium and being at least moderately soluble in said sol precursor, said volatile liquid bloating agent being added to said sol precursor as droplets or microdroplets at a pressure in the range 39.2 kPa to 107.9 kPa. The process provides microbubbles having encapsulated therein gases or combinations of gases depending on the conditions under which the bubbles are formed.

Preferably the bubble promoting medium used in the process of the invention is a liquid such as an aliphatic alcohol, e.g. oleyl alcohol, or a long chain carboxylic acid ester such as peanut oil, or mixtures thereof, or mixtures of oleyl alcohol with other vegetable oils or vegetable oil derivatives.

Adding a source of carbon such as wood cellulose to the gelled microbubbles serves to:

- a) prevent agglomeration of bubbles during processing, and
- b) assist in converting the microbubbles to non-oxide containing microbubbles by providing a carbon source.

When the firing of the gelled or green ceramic microbubbles takes place in the presence of an inert or reducing atmosphere and at a sufficiently high temperature, the green, oxide containing ceramic microbubbles can be converted into non-oxide containing ceramic microbubbles; the preferred atmosphere is nitrogen or argon.

The green microbubbles can be fired, optionally in the presence of an agglomeration preventative agent, to provide the ceramic microbubbles of the invention.

A firing temperature range significantly below, preferably about 300 °C below, that range known in the art to convert oxide containing ceramics to non-oxide containing ceramics can be used.

The ceramic bubbles may also be referred to as thin-walled, hollow, microspheres and are useful as abrasives, catalyst supports, insulating materials and the like.

As used in this application:

"sol precursor" or "sol-gel precursor" means a liquid (solution or dispersion or mixture thereof) which can contain metal salts, basic metal salts, hydrolyzable metal complexes such as alkoxides, colloidal dispersions of inorganic solids such as oxides, hydroxides, oxy-hydroxides or mixtures thereof, and adjuvants such as film forming agents;

"ceramic" means any inorganic nonmetallic material (including metal oxides, carbides, and nitrides) which requires the application of high temperatures at some stage in its manufacture;

"essentially all oxide or non-oxide" means that by standard powder X-ray diffraction analysis only the oxide or non-oxide phase is detected.

"sol-gel" is a term used in the ceramic art and is applied to the preparation of ceramics from sol or solution precursors or combinations thereof;

"film forming agent" means any chemical substance, generally a polymer, which, when added to a sol precursor or mixtures thereof, induces film formation during removal of solvent; that is, the surface of the liquid increases in viscosity during removal of solvent resulting in a skin or film on the surface. It is believed that upon removal of solvent the induced concentration of the film forming agent at the solution surface causes an increase in viscosity that forms the "skin" or film;

"adjuvants" means substances which may be present in the inventive compositions including fluxing agents such as soda (e.g., introduced as sodium carbonate), boria, or phosphorus pentoxide and fugitive polymeric additives such as methylcellulose in the precursor mixtures which can help to generate more uniformity of wall thickness and size in bubble formation;

"bloating agent" means any liquid having a boiling point at or below the temperature of the bubble promoting medium, having high solubility or miscibility in the sol precursor, and which induces rapid expansion of the nascent bubbles upon heating;

"non-vitreous" means that a ceramic has not been derived from a melt or mixture of raw materials brought to the liquid state at high temperature, such as in a molten glass. As used, this term distinguishes the inventive ceramic hollow microspheres over glass composition bubbles which are made by a melt process;

"fired" or "fired solids" means the actual oxide equivalent, the weight percent of which is obtained by weighing a sample, drying and firing it to a temperature sufficient to remove fugitive components and to convert to the oxide, e.g., at a temperature of 400 °C and above, preferably in the range of 600 °C to 1000 °C, to remove water and organic substances and any other volatile components, weighing the fired

sample and dividing this fired weight by the initial sample weight and multiplying the quotient by 100;

"transparent" means that the walls of the fractured hollow ceramic microbubbles or spheres when viewed under an optical microscope (e.g., at 100X), have the property of transmitting rays of visible light so that bodies beneath the microbubble wall, for example, such as bodies having essentially the same nature as the microbubbles, can be clearly seen through the walls of the microbubbles. A recommended procedure would be to observe the bubble fragments submerged in clear oil. The refractive index of the oil should not be so close to that of the walls of the hollow microbubbles such that they seem to disappear (as would be the case of a perfect index match). When whole intact bubbles are examined under the microscope, the hollow space inside the bubbles appears dark because of the mismatch of the refractive index of air and oil.

Not all bubbles of this invention are transparent or even translucent. Many, for example those of predominantly carbide-containing compositions, are opaque;

"fully dense" means that walls of the bubbles are close to theoretical density and having substantially no open porosity (i.e. less than 4 volume percent pores) detectable by standard analytical techniques such as the B. E. T. nitrogen technique (based upon adsorption of nitrogen molecules from a gas with which a specimen is contacted). Such measurements yield data on the surface area per unit weight of a sample (e.g. m^2/g). Density can be measured on wall fragments by mercury pycnometric or porosimetry procedures. Higher specific surface (m^2/g) indicates higher surface irregularities and/or porosity. Surface area and porosity measurements may be made on a Quantasorb™ apparatus made by Quantachrome Corporation, Syosset, New York;

"grain" means 1) crystallites in crystalline materials, and 2) domains or colloidal particles in amorphous materials;

"microstructure" means the structure and size of the primary crystallites which make up a ceramic body and the packing of these crystallites into arrays and the structure of such arrays and three dimensional networks derived from the crystallites. A fine "microstructure" indicates that the material is composed of very small crystallites (generally about 1 micrometer in diameter or less in the case of equiaxed crystallites);

"equilibrium boiling point method" means a method for forming the microbubbles wherein a sol precursor, in the form of droplets which is mixed with, or contains a certain amount of a low boiling liquid, referred to as a bloating agent, is atomized and added dropwise into a hot, stirred liquid bubble promoting medium; after a certain period of time depending on the sol droplet size, those droplets reach the equilibrium boiling point and the gel particles bloat as the gases inside expand. When the density of the bloated bubbles falls below the density of the bubble promoting medium, the equilibrium boiling point has been reached and the particles rise in the bubble promoting medium and float on the surface thereof;

"green" means an unfired gelled article convertible to a ceramic article by firing; and

"agglomeration preventative agent" means a decomposable carbon containing compound which may be in bulk form or mixture of compounds which is admixed with the green gelled microbubbles of the invention prior to firing; the presence of such an agent prevents cohesion of the microbubbles.

Sol precursors useful for preparing the oxide component (if used) of ceramic microbubbles of the present invention are well known in the art and include those for preparing alumina, alumina-magnesia, barium titanate, mullite, alumina-silica (U.S. Patent No. 4,047,965), alumina-boria and alumina-boria-silica (see U.S. Patent No. 3,795,524), titania (U.S. Patent No. 4,166,147), silica, zirconia, zirconia-silica (U.S. Patent Nos. 3,709,706 and 3,793,041), zirconia-yttria, zirconia-magnesia, zirconia-calcia, zirconia-ceria, and other zirconia-containing materials (U.S. Patent No. 4,772,511), thoria-silica-metal (III) oxide (U.S. Patent No. 3,909,278) and alumina-chromia-metal (IV) oxide (U.S. Patent No. 4,125,406).

Representative examples of such sol precursors include zirconyl acetate, aluminum formoacetate, tetraisopropyl titanate, and those disclosed in U.S. Patent No. 4,349,456. Sol precursors useful for preparing non-oxide containing ceramic microbubbles may also include those containing metal and non-metal nitride and carbide colloidal particles. Concentration of the sol precursor will depend on the nature of the sol ingredients but will generally be in the range of 9 to 22 weight percent solids. Density of the sol precursor can be in the range of 1.1 to 1.5 g/cc. Viscosity of the sol precursor can be in the range of 50 to 1000 cP, preferably in the range of 500 to 800 cP.

A bloating agent for use in the present invention includes any liquid added to the sol precursor or its mixtures, which induces bloating or expansion of the droplet upon heating. This expansion is believed to be the result of the rapid formation of a gas or vapor which is composed mainly of the vaporized bloating agent within the nascent gel bubble. The bloating agent is characterized by a boiling point below the temperature of the bubble promoting medium and a moderate to high solubility or miscibility in the sol precursor or its mixtures. Any volatile compound having a boiling point at or below the temperature of the bubble promoting medium can be useful in the formation of the microbubbles. Representative examples include liquids which

boil in the range of 25 to 100°C at atmospheric pressure (760 Torr) and include halocarbons such as chloroform, aldehydes such as formaldehyde, ethers, alcohols such as ethanol and methanol, and ketones such as acetone and methyl ethyl ketone, and combinations thereof such as a mixture of liquid halocarbons (e.g. Freon™ 11, Dupont, Wilmington, DE and Genetron™ 11, Allied Chemical Co., Morristown, NJ) and methanol (1/1 vol/vol). Preferred bloating agents include acetone, and a (1/1 vol/vol) liquid Freon 11 and methanol mixture.

A bloating agent useful in the present invention exhibits complete volatility at or below the gel-forming temperature in the equilibrium boiling point method of this invention. Suitable bloating agents include organic liquids having a boiling point below that of the bubble promoting medium and miscible with the sol precursor. The bloating agent or mixtures thereof has solubility or miscibility (of at least 5 wt. percent) in the sol precursor. The miscibility or solubility of the bloating agent can be affected by choice of the liquid used in the precursor.

A bubble promoting medium for use in the present invention refers to a liquid at the temperature of bubble formation, to which a mixture of the sol precursor and bloating agent is added with subsequent conversion to bubbles by the equilibrium boiling point process and wherein the bubbles become rigid during the sol-gel process. Useful bubble promoting media include esters of long chain fatty acids having at least 8 carbon atoms, vegetable oils, such as corn oil, safflower oil, soybean oil, sunflower oil, peanut oil, and various derivatives of these oils and combinations thereof, and long chain alcohols having at least 8 carbon atoms and up to 20 carbon atoms such as oleyl alcohol, and mixtures thereof and combinations of any of these carboxylic acid esters, alcohols and oils. Especially useful bubble promoting media are oleyl alcohol and mixtures of oleyl alcohol with peanut oil, especially a 1/1 (vol/vol) mixture thereof.

Sol-gel processes for preparing shaped ceramic articles are well known in the art and have been taught in the art; see for example U. S. Patent Nos. 4,349,456, 3,709,706, and 4,290,847. Generally, a sol-gel process is one which converts a colloidal dispersion, sol, aquasol, or hydrosol of a metal oxide, or precursor thereof, to a gel. A gel is a material wherein one or more of the components are crosslinked either chemically or physically to such an extent as to cause a three dimensional network to form. The formation of this network results in an increase in viscosity of the mixture and a mechanical immobilization of the liquid phase within the network. The sol-gel process also has the advantage of enabling the use of a lower processing temperature than glass bubble forming processes and thus requires less energy consumption per unit weight produced.

In the method of the present invention, high quality, thin-walled, green ceramic microbubbles are produced by a sol-gel process which exploits the phenomenon of formation of these microbubbles by adding dropwise a mixture of sol precursors and a liquid bloating agent to a bubble promoting medium and controlled gelation of the resultant microbubbles (equilibrium boiling point method). We have found that a combination of pressurized air (in the range of 39.2 kPa to 107.9 kPa (0.4 to 1.1 kg/cm²)) and pressurized sol precursor (in the range of 39.2 kPa to 107.9 kPa (0.4 to 1.1 kg/cm²)) results in the sol precursor forming micro size (e.g., less than 200 micrometers) droplets when sprayed through an atomizing nozzle as is known in the art. The ratio of sol to bloating agent depends on the nature of the sol. Generally, the ratio, in parts by volume of sol precursor to bloating agent can be in the range of (70 to 99) : (1 to 30). The ratio of sol precursor to bubble promoting medium can be the range of (1 to 20) : (80 to 99) parts by volume.

The gelling step is often followed by drying the formed microbubbles to provide a green (unfired) product and then firing the green microbubbles to provide a refractory ceramic material stable at high temperatures.

We discovered that a sol precursor droplet, which contains a certain amount of a low boiling liquid (referred to as a bloating agent) such as acetone or ethanol preferably 1:1 vol/vol liquid halocarbon and methanol, bloats or becomes a bubble when dropped into a hot liquid (referred to as a bubble promoting medium). We further discovered that if the droplet is induced to gel concurrently with bloating, the resultant green, gelled bubbles are obtained, which, when isolated and fired, provide strong, well formed ceramic microbubbles.

Gelling can be induced by one or a combination of methods the choice of which depends on the nature of the precursor solution. Often, as is taught in U.S. Patent No. 4,349,456, sols containing basic metal salts can be dehydratively gelled, that is through removal of water from the sol droplet by the forming medium. As is disclosed in U.S. Patent No. 2,689,226, incorporation of an adjuvant in the sol precursor such as hexamethylenetetramine which will thermally decompose to generate ammonia can be utilized in certain systems to gel the nascent bubble. Other methods to induce gelation include addition of a weak base as is taught in U.S. Patent No. 2,666,749 and controlled removal of the metal counterion (see, for example, J. L. Woodhead and D. L. Segal Br. Ceram. Proc., 36 (1985) 123-128). Variations and limitations of these techniques are apparent to those skilled in the art.

While not being bound by theory, it is believed that droplets or microdroplets of a mixture of the sol precursor with a liquid bloating agent, on addition to a temperature controlled bubble promoting medium, bloat and become microbubbles. It is believed that the low boiling bloating agent, on contact with the hot bubble promoting medium, vaporizes, and the resultant vapors or gases cause bubble formation. This overall process is referred to as the equilibrium boiling point method.

In a preferred embodiment, the immersion of a droplet comprising a mixture of bloating agent and sol into hot oleyl alcohol (bubble promoting medium) produces high quality green microbubbles. The present invention provides bubbles filled with gas (e.g. air, gas, vapor, and the like), rather than bubble promoting medium. Walls of the green hollow microbubbles can be made fully dense by firing the green microbubbles to a sufficiently high temperature.

In the gelation process, the bubble promoting medium is desirably characterized by: low solubility (e.g. less than 1 weight percent) for the sol precursor and other sol ingredients including adjuvants; a reasonable degree of stability within the temperature range of use; inertness to chemical precursors (e.g. sol precursors, adjuvants, agglomeration preventative additive, etc.) of the resultant ceramic; and a possibility of recovering (by appropriate processing, e.g., to remove water, acetic acid and the like) and recycling the medium.

The temperature of the bubble promoting medium is maintained in the range of 50 to 150 °C, preferably 80 to 100 °C, most preferably at 90-97 °C. (all temperatures stated in this invention are in degrees Centigrade unless indicated otherwise). Preferably the bubble promoting medium is oleyl alcohol. Mixtures of oleyl alcohol with oils such as vegetable oil, corn oil, safflower oil, soybean oil, sunflower oil, peanut oil and various derivatives of these oils can also be used. A mixture of oleyl alcohol with peanut oil is a convenient medium.

The bubble promoting medium can be recovered after microbubble formation by filtration, regenerated by heating the resultant filtrate briefly above about 118 °C (for example to remove water and residual acetic and formic acids from sol precursors such as metal acetates and metal formoacetates), and then used for bubble formation.

To prepare mullite-containing ceramic microbubbles for example, a sol precursor, comprised of a mixture of basic aluminum carboxylate, colloidal silica, and an adjuvant such as a stabilizing agent (e.g. lactic acid as described in U. S. Patent Nos. 3,795,524 and 4,047,965 on aluminum borosilicate fibers), is generally concentrated (typically to about 20 weight percent fired solids) prior to the addition of a second mixture comprised of a bloating agent and optional adjuvants which can include a film-forming agent, such as methyl cellulose (Methocel™ Dow Chemical Co., Midland, MI) or polyvinylpyrrolidone such that the resultant mixture has a convenient density and viscosity (e.g. density = 1.1 to 1.5 g/cc, preferably about 1.2g/cc and the viscosity is in the range of 50 to 1000 cP, preferably about 500 cP) to allow droplet or microdroplet formation when this mixture is added through an atomizer into a bubble promoting medium.

Adjuvants such as colorants, film forming agents, and stabilizing agents, can be present in the sol precursor or bloating agent in an amount in the range of 0 to 10 weight percent of the sol precursor.

Concentration of mixtures described above can conveniently be accomplished by evaporation in a evacuated rotating flask using commercial roto-evaporators (e.g. Buchi/Brinkmann rotary evaporator, Westbury, NY). Briefly, rotoevaporation involves evaporating a liquid from an externally heated rotating vessel into a cooled receiving flask, often conducted under reduced pressure.

A mixture, comprised of sol precursor, adjuvants such as film forming agent, and bloating agent is added, as droplets or microdroplets, to a heated bubble promoting medium. Any means to form the above droplets is suitable such as spraying, atomizing, addition via syringe, and other means known in the art. The microbubbles are best formed by atomizing. By atomizing is meant breaking the sol precursor into micro-size droplets by a combination of pressurized air, about 39.2 kPa to 107.9 kPa (0.4 to 1.1 kg/cm²), preferably 68.6 kPa (0.7 kg/cm²) and pressurized sol precursor, about 39.2 kPa to 107.9 kPa (0.4 to 1.1 kg/cm²), preferably 49 kPa (0.5 kg/cm²) when sprayed through an atomizing nozzle.

As the droplets are introduced into the heated bubble promoting medium, a concomitant combination of bloating of the droplets and gel formation provides green microbubbles.

The resultant gelled or green microbubbles can be removed from the bubble promoting medium by filtration (the bubble promoting medium filtrate can be recycled), and fired to provide ceramic microbubbles. Preferably, the bubbles are first washed with a suitable organic solvent such as ethanol (for the purpose of removing residual bubble promoting medium), mixed with a source of pure wood cellulose such as commercial SolkaFloc™ (James River Corp., Berlin, NH) and this mixture is then fired in an oxidizing atmosphere (air for example). Firing of the resultant bubbles to a temperature sufficient to cause densification produces sturdy, spherical, transparent, thin-walled, impermeable (i.e., essentially resistant to flow or diffusion of fluids) ceramic bubbles.

Depending upon the particular sol precursor and firing temperature used, walls of the fired ceramic bubbles can be porous and heat sealable or dense and impermeable. Any metal oxide in the bubble walls is present in whole or in part in the polycrystalline state or in an amorphous state capable of conversion, upon further firing, to the polycrystalline state. Higher temperatures can act to make, the bubble walls impermeable by sealing off porosity or by densification.

In general, higher firing temperatures in the range of 1000°C to 1400°C help to achieve hollow microbubbles with fully dense walls. In the firing process, these bubbles are loosely packed with a source of carbon to obtain a uniform, free flowing fired product. The carbon source, preferably in the form of wood cellulose which is free of undesirable impurities such as sulfur, can act as a reducing agent for the conversion of oxide to non-oxide ceramic.

We have also found that the sintering temperatures of these sol-gel derived ceramic bubbles are hundreds of degrees below the temperatures that are required to convert conventional ceramic powder processed products to crystalline and dense ceramics as heretofore taught in the art. For example, the carbothermal reduction of TiO_2 by carbon followed by nitriding with nitrogen and/or ammonia gas has been shown to require high temperatures, e.g. 1600°C (see for example, M. Yoshimura, M. Nishioka, and S. Somiya, *J. Mater. Sci. Lett.* 6 1463 (1987)). By following the procedure described herein we have prepared fully converted, fine microstructured titanium nitride ceramic bubbles from titania microbubbles at a temperature below 1400°C.

As already discussed, certain parameters can be considered and optimized to obtain well-formed hollow microbubbles. For example, concentration and hence, viscosity, of the mixture comprising the sol precursor, bloating agent, film forming agent, and other adjuvants, temperature range of the bubble promoting medium, and manner of addition of the mixture, in droplet form, to the bubble promoting medium can be varied in order to determine the optimum process to derive ceramic bubbles of a certain selected average diameter and wall thickness. Optimum values for these parameters can vary for different sol-gel precursors and their mixtures; that is, conditions to produce alumina-boria-silica microbubbles will not necessarily be the same as those for alumina-magnesia microbubbles. By choice of the proper conditions for these parameters, one can provide well-formed, spherical microbubbles having a single central cavity with walls of relatively uniform thickness. The term "relatively uniform" in this invention means that the wall thickness does not vary by more than 2% of the bubble diameter.

As previously described, viscosity of the sol precursor mixture would be in the range of 50-1000 cP. This viscosity range will limit the solid concentration range which can be used for a particular sol mixture. In general, raising the solids concentration is accompanied by an increase in viscosity. Use of higher solids concentrations or higher viscosity sols results in thicker walls and smaller diameters for bubbles generated from a particular precursor droplet size.

Concentration of the bloating agent can also be varied so as to change the size and wall thickness of the bubbles generated for a particular precursor droplet size. For constant sol concentration and droplet size, increasing the bloating agent concentration increases the average diameter and decreases the average wall thickness of the resulting bubbles. The ratio in parts by volume of sol precursor to bloating agent can be in the range of (70 - 99) : (1 - 30).

Temperature of the bubble promoting medium affects the size, wall thickness and quality of the inventive bubbles. Up to a certain limit, raising the temperature of the bubble promoting medium results in larger, thinner walled bubbles. This temperature limit depends on the concentration of the sol, nature of the sol and concentration of the bloating agent. Exceeding this temperature limit results in an increase in the percentage of broken bubbles in the final product. Raising the concentration of the bloating agent lowers this temperature limit. In general, raising the sol concentration raises this temperature limit. Further addition of various polymeric additives or film forming agents to the sol precursor can also raise this temperature limit. Temperature of the bubble promoting medium is maintained at 50 to 150°C, preferably 80-100°C, and most preferably at 90-97°C.

To improve the physical and mechanical properties of the ceramic microbubbles produced by the method of this invention, defects or flaws in the form of broken bubbles and holes should be prevented. Imperfections in the form of holes can be minimized by gelling the bubbles before the bubbles are allowed to contact each other. Bubbles can be broken by exposing the bubbles to an excessively high temperature of the bubble promoting medium or by incorporating an excess of the bloating agent, or a combination thereof.

Annealing and heat treatment steps in the hot bubble promoting medium assist in yielding intact, denser, and stronger gel bubbles by allowing the nascent, individual gel bubbles to gel completely as separate particles in the hot bubble promoting medium before contacting other particles during separation. The gelled bubbles need to be annealed at lower temperatures (e.g., about 60-80°C) after the bubble

generation. After the annealing step, the bubbles are hardened by exposure to higher temperatures, e.g., 80°C up to 115°C, before separating the bubbles from the bubble promoting medium.

Wall thickness of the bubbles can be controlled by a combination of suitable bloating agent, concentration, and viscosity of the sol precursor mixture; these parameters having been discussed above. Wall thickness can be measured by scanning electron microscopy (SEM) or transmission electron microscopy (TEM).

Microbubbles of the invention can be formed by the equilibrium boiling point method. Temperatures which are suitable for the equilibrium boiling point method are dependent on the nature of the bloating agent, concentration of the bloating agent, concentration of the sol precursor, the manner in which the sol precursor gels, and the physical characteristics of the bubble promoting medium. Preferably, the temperature will be in the range of 80-100°C, most preferably in the range of 90-97°C.

In the process of this invention, a reducing agent, e.g., a source of carbon such as wood cellulose can optionally be mixed with the green bubbles prior to the firing step. The firing step can be carried out, for example, in an argon or a nitrogen atmosphere or in a mixture of the two gases. Any atmosphere may be used that will not be detrimental to the conversion of the gelled microbubbles to the desired non-oxide ceramic microbubbles. Where non-oxide bubbles are desired, those containing less than 5% oxide are preferred.

More particularly, we have discovered that green oxide-containing microbubbles prepared as described above, when fired in a bed of wood cellulose powder in the presence of a reduction supporting atmosphere of noble and certain reactive gases such as argon, xenon, neon, helium, or nitrogen or mixtures thereof yield electrically conductive, fine microstructured (as determined by SEM) non-oxide ceramic microbubbles. They are mostly in the form of carbides and nitrides. By reduction supporting atmosphere is meant any atmosphere which supports or at least is not detrimental to the conversion of oxide containing ceramics to non-oxide containing ceramics. X-ray diffraction (XRD) results show that a mixture of oxides and carbides, for example, in the case of ceramic bubbles derived from zirconyl acetate and using wood cellulose as a reducing agent, a mixture of ZrC and ZrO₂ is produced below 1480°C in an argon atmosphere. Above that temperature, the only crystalline phase detected was zirconium carbide.

When unfired or green titanium oxide containing microbubbles, prepared as described above, were fired in a bed of wood cellulose powder in the presence of a nitrogen atmosphere, there was obtained electrically conductive, fine microstructured (as determined by SEM) ceramic microbubbles of titanium nitrides. X-ray diffraction results revealed that a mixture of nitrides and oxides was produced below 1420°C in a nitrogen atmosphere, and above that temperature, the only crystalline phase detected was titanium nitride.

Non-oxide microbubbles of this invention have the following general characteristics: diameter of about 1-300 micrometers; electrical resistivities of about 0.02-0.2 ohm.cm (as measured by a Simpson Ampere meter (Simpson Electric Co., Chicago, IL), and are colored, depending on the composition. The walls can be fully dense with smaller than 0.1 micrometer grains or crystallites. For example, titanium carbide is black and non-transparent and both titanium nitride and zirconium nitride are gold colored.

While not being bound by theory, it is believed that during firing of the green or oxide containing ceramic microbubbles in the presence of both a reduction supporting atmosphere and a source of carbon such as wood cellulose, the wood cellulose is reduced to carbon or a carbon-containing intermediate phase, which causes conversion of the green or oxide containing ceramic microbubbles to non-oxide containing ceramic microbubbles.

We have further discovered that firing temperatures to effect this conversion occur at about 300°C below those firing temperatures necessary to convert a mixture of usual oxide-containing ceramic powder with powdered carbon to non-oxide-containing ceramic powder. Moreover, scanning electron microscope (SEM) micrographs showed that the sizes of individual crystallites present in the bubble wall of microbubbles of this invention were smaller than 0.1 micrometers and X-ray diffraction (XRD) studies revealed that the only crystalline phase found in the bubbles was nitride (e.g., TiN, formed at a firing temperature of 1360°C, and ZrN, 1420°C) or carbide (TiC, 1420°C; ZrC, 1480°C). Electrical resistivity (reported in ohm times cm, ohm.cm) of various non-oxide ceramic microbubbles, firing temperature, and reduction supporting atmosphere are summarized in Table 1.

Microbubbles of this invention are typically uniform in shape and wall thickness, transparent, tough, durable, highly resistant to scratching, chipping, and cracking.

Voids in the walls of the hollow microspheres of the invention are desirably averted, by firing the gelled microsphere precursors to a dense state at a temperature of 600°C or higher. This improves transparency, prevents both structural gaps or defects and any accompanying weakening effects and absorption of moisture or other liquids that can degrade the microspheres. In general, higher firing temperatures promote densification of the walls of the ceramic microspheres. Depending on the particular oxide precursor material

and firing temperature used, the walls of the fired ceramic bubbles will be porous and heat-sealable or impermeable. In general, the temperature required to seal the non-oxide bubbles will be higher than that required to seal the oxide bubbles. For example, TiO_2 bubbles can be sealed at temperatures in the range of 600 to 700 °C. Titanium nitride can be sealed at about 1360 °C.

Pressure within the sealed microbubbles will be dependent upon the temperature at which sealing is accomplished and the pressure of the select gas at that temperature. Thus, the pressure of the select gas and its pressure within the sealed microbubbles can be varied over a wide range, from sub-atmospheric (vacuum) to super-atmospheric, i.e., from 0.0001 to 2.0 or more atmospheres, preferably 0.5 atmospheres to 2.0 atmospheres (380 to 1520 Torr), and predetermined or approximated according to the gas laws. This process allows encapsulation of very pure gases and preselected combinations of gases.

Microbubbles of this invention may be truly spherical but they may be slightly oblate or prolate. Generally, they are spherical. Preferred ceramic microbubbles are also generally characterized by: diameters in the range of 1-300 micrometers, wall thickness preferably in the range of 1-8 percent of the diameter of the microbubble, smooth surface and density of 0.3 to 0.6 g/cm³. By smooth surface is meant that the surface roughness is less than 2500 Angstrom units where surface roughness is defined as the average height of repeating or regular surface protuberances as measured vertically from the bottom to the apex of the protuberance using scanning electron microscopy (SEM).

Most metal oxides form a polycrystalline or microcrystalline phase. Additives such as yttrium oxide can form solid solutions with other oxides, such as zirconia, resulting in the stabilization or partial stabilization of the metal oxide (e.g. zirconia in the cubic or tetragonal form).

As taught in U. S. Patent No. 4,349,456 and applicable in this invention, hydrogen or other reducing atmosphere can be used where desired to form ceramic microbubbles comprising reduced metal oxides, e.g. ferrous oxide, or metals, e.g. iron. Inert atmospheres, e.g. argon, nitrogen, xenon, neon, or helium, can be used, particularly where it is desired to form ceramic microbubbles with such inert atmospheres filled and heat-sealed therewith. Generally, where it is desired to form sealed ceramic microbubbles with a vacuum or select gas (other than air) encapsulated therein, it will be convenient to use an air atmosphere to convert the dried, gelled microbubbles to porous ceramic microbubbles and then heat-sealed by firing the latter at a high enough temperature, in a range from 500 ° to 1400 °C depending on the ceramic, to render the porous wall impermeable in a vacuum or an atmosphere of the select inert gas as noted above. The resultant bubbles will contain the vacuum or selected gas within its single cavity. Ceramic bubbles containing a reducing atmosphere (e.g., carbon monoxide or hydrogen) can also be prepared by firing in the appropriate atmosphere. During the firing stages, if oxygen is present, the surface of the bubbles can be made to be oxygen-rich.

Table 1

Electrical Resistivity of Non-oxide Ceramic Microbubbles			
Bubble composition*	Firing Temp. (°C)	Atmosphere	Resistivity (ohm-cm)
TiC	1420	Argon	0.02
TiN	1420	Nitrogen	0.05
ZrC	1480	Argon	0.20
ZrN	1420	Nitrogen	0.09

* all bubbles had grain size less than 0.1 micrometer

Some firing conditions and crystallite characteristic of some bubbles of this invention are given in Table 2.

TABLE 2

Starting Materials	Firing Conditions	Crystallite Phases	Crystallite Size (μm)	Resistivities ($\Omega\cdot\text{cm}$)
zirconyl acetate gel bubbles (ϕ : 20-100 μm , thickness: 0.2-1 μm)	1360°C, 2 hrs Ar atmos N ₂ atmos	ZrC ¹⁰⁰ , ZrO ₂ (T) ⁶⁰ , ZrO ₂ (M) ¹⁹ ZrN ¹⁰⁰ , ZrO ₂ (T/C) ⁵		
	1420°C, 2 hrs Ar atmos N ₂ atmos	ZrC ¹⁰⁰ , ZrO ₂ (T) ⁸ , ZrO ₂ (M) ³ ZrN	0.5-1 <0.1	0.2 0.09
	1480°C, 1 hrs Ar atmos	ZrC	<0.1	0.2
	1480°C, 2 hrs N ₂ atmos	ZrN	<0.1	0.09
	1480°C, 2 hrs Ar atmos	ZrC ¹⁰⁰ , ZrO ₂ (M) ⁷⁴	0.5-1	
without cellulose fiber powder	N ₂ atmos	ZrO ₂ (C) ¹⁰⁰ , ZrN ⁷⁴ , ZrO ₂ (M) ⁴¹	~1.5	
TiO ₂ gel bubbles (ϕ : 20-100 μm , thickness: 0.2-1 μm)	1360°C, 2 hrs Ar atmos N ₂ atmos	TiC ¹⁰⁰ , Ti ₂ O ₃ ²² TiN		
	1420°C, 2 hrs Ar atmos N ₂ atmos	TiC TiN	<0.1 <0.1	0.02 0.05
	1480°C, 2 hrs Ar atmos N ₂ atmos	TiC TiN	<0.1 <0.1	0.02 0.02

TABLE 2 (cont.)

Starting Materials	Firing Conditions	Crystallite Phases	Crystallite Size (μm)	Resistivities ($\Omega\text{-cm}$)
$\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$ gel bubbles (ϕ : 20-100/ μm , thickness: 0.02-1/ μm)	without cellulose fiber powder 1480°C, 30 min. N_2 atmos	$\alpha\text{-Al}_2\text{O}_3$, TiN^{76}	-0.5	
	with cellulose fiber powder 1750°C, 1 hr N_2 atmos.	TiN^{100} , AlN^{35}	<0.1	
ϕ : diameter,	$\text{ZrO}_2(\text{M})$: Monoclinic,	$\text{ZrO}_2(\text{T})$: Tetragonal,	$\text{ZrO}_2(\text{C})$: Cubic	

Articles comprising microbubbles of this invention can be fabricated into useful three dimensional shapes. For example, combining the microbubbles of this invention with various binder materials such as water glass, polymers such as epoxy resins, and sol-gel derived binders can provide low density structural reinforcement composites, catalyst substrates, machinable refractories, and supports. In addition, the microbubbles can be used as carriers for drugs and the like for applications where controlled release is desired.

Objects and advantages of preferred embodiments of this invention are further illustrated by the following non-limiting examples.

Examples 1-3 describe non-oxide containing microbubbles.

Example 1 is representative for the preparation of non-oxide-containing microbubbles and details for their preparation are conveniently summarized in Table 2.

EXAMPLE 1

Zirconyl acetate (100 g; Harshaw-Filtro, Cleveland, OH) was diluted with water to make a 15 % fired solids solution. Polyvinylpyrrolidone (18 g, 5% solution; PVP-K30™, General Aniline & Film Corp., New York, NY), 16.5 g of acetone, and 1.5g of Methocel were added with stirring to 167 g of the diluted acetate sol. The mixture was covered with Parafilm and stirred until the initial white floc which formed dissolved. This sol was broken up by atomization and was sprayed into hot (95°C) oleyl alcohol. The atomizer was positioned 9.5 cm (3.75 inches) from the surface of the hot oleyl alcohol. The droplets formed small bubbles and floated on the surface of the oleyl alcohol. The stirred mixture was maintained at 95°C for 15 minutes. The gelled bubbles were separated by filtration, washed with ethanol and mixed with cellulose fibers (Solka-Floc™ SW40, James River Corporation, Berlin, NH) at the wt. ratio of 1/4 before refiltration and drying at 80°C for 2 hours. Those mixtures of gel bubbles (ZrO₂ composition) and Solka-Floc powders were placed in a graphite mold (closed system) and fired to 1420°C and 1480°C in N₂ and Ar atmospheres by a controlled schedule (room temperature up to 1200°C over a period of 2 hours, then 1200°C up to 1420°C and 1480°C, respectively, over a period of 1.5 hours) and held at these temperatures for 2 hours. The samples were then allowed to cool with the furnace. XRD results of these samples showed that the only crystal phases found in the samples (ZrO₂ base bubbles fired to 1420°C and 1480°C in N₂ and Ar atmospheres) were ZrN and ZrC respectively. Examination with a SEM revealed that the size of individual crystallites present in the walls of bubbles of diameters 20-100 micrometers and wall thickness of 0.2-1 micrometer was smaller than 1/10 micrometer for the bubble samples with the nitride or carbide phases. Electrical resistivities of ZrN bubbles and ZrC bubbles, prepared by this method were 0.09 and 0.20 ohm-cm respectively. The colors of nitride bubbles fired to 1420°C for 2 hours were gold and carbide bubbles fired to 1480°C were black.

EXAMPLE 2

DMF (dimethylformamide, 10 g) and acetone (10 g) were added with stirring to a mixture of 77.5 g of aluminum formoacetate (9.5% aluminum oxide) [for preparation see Kirk-Othmer, Encyclopedia of Chemical Technology, third ed., Vol. 2, 202-204 (1978)] and 32 g of titanium lactate sol (TYZOR LA™; E. I. duPont de Nemours & Co. Inc., Wilmington, DE). The resulting mixture was covered with Parafilm and stirred until the initial white floc which formed dissolved. This sol was broken up by atomization and was sprayed into hot (95°C) oleyl alcohol. The atomizer was again positioned 9.5 cm (3.75 inches) from the surface of the hot oleyl alcohol. The droplets formed small bubbles and floated on the surface of the oleyl alcohol. The stirred mixture was maintained at 95°C for 15 minutes. The gelled bubbles were then mixed with Solka-Floc in oleyl alcohol and the mixture was separated by filtration, placed in a BN crucible and fired to 1750°C under N₂ atmosphere according to a controlled schedule (room temperature up to 1000°C over a period of 20 min., then 1000°C up to 1750°C at the rate of 25°C/min.) and held at this temperature for 1 hour. The sample was then allowed to cool with the furnace. Examination with a microscope revealed that a large fraction of the bubbles were 20 - 100 micrometers in diameter with wall thicknesses of 1 - 2 percent of the total diameter and were intact. SEM micrographs showed that the sizes of individual crystallites present in the wall of this bubble sample were smaller than 1/10 micrometer. XRD analysis of this bubble sample revealed that the crystal phases in the sample were TiN and AlN.

EXAMPLE 3

DMF (10 g) and acetone (10 g) were added with stirring to the mixture of 78 g of aluminum formoacetate (9.5% aluminum oxide) [for preparation see Kirk-Othmer, Encyclopedia of Chemical Technology, third ed., Vol. 2, 202-204 (1978)] and 32 g of titanium lactate sol (TYZOR LA). The resulting mixture was stirred for approximately 30 minutes and then injected into 90-95°C oleyl alcohol using an atomizer with 69 KPa (10 psi) air pressure. The droplets formed small bubbles and floated on the surface of the oleyl alcohol. The stirred mixture was maintained at 95°C for 15 minutes. The gelled bubbles were separated by filtration and fired to 1480°C for 30 minutes in N₂ atmosphere. XRD analysis of these bubbles showed that

Al_2O_3 and TiN phases were present in the sample.

The zirconia gel bubbles produced in Example 4 were fired to 1480°C for 2 hours in N_2 and Ar atmospheres without aid of Solka-Floc or carbon black powder. The crystalline phases found by XRD analysis in the sample fired to 1480°C in an argon atmosphere were ZrC and monoclinic ZrO_2 and in the sample fired to 1480°C in nitrogen atmosphere were cubic zirconia, zirconium nitride, and monoclinic zirconia.

Claims

- 10 1. Free-flowing, discrete ceramic microbubbles consisting essentially of either 1) a non-oxide ceramic component and an oxide ceramic component, or 2) non-oxide ceramic, each microbubble having a fine microstructured ceramic wall and a single central cavity, said microbubbles having a diameter in the range of 1 to 300 micrometers and a wall thickness of less than 10 percent of the diameter of the microbubbles.
- 15 2. Microbubbles according to claim 1 wherein the ratio of said non-oxide ceramic component to said oxide ceramic component is in the range 95:5 to 5:95 parts by weight.
- 20 3. Microbubbles according to either of claims 1 and 2 wherein said ceramic comprises at least one of a metal nitride, a metal carbide, and a metal oxide.
- 25 4. Microbubbles according to any of claims 1 to 3 wherein said cavities are a vacuum or said cavities contain a gas.
5. Microbubbles according to any of claims 1 to 4 wherein said ceramic walls are selected from the group consisting of aluminum-, titanium-, zirconium-, and silicon-containing ceramics.
6. A shaped article comprising microbubbles according to any of claims 1 to 5.
- 30 7. A method for providing green microbubbles comprising the steps of:
 - a) adding a mixture comprising of sol precursor and a volatile liquid bloating agent to a bubble promoting medium at a temperature in the range from 50 to 150°C to provide green, hollow, microbubbles, said sol precursor comprising either
 - 35 i) a non-oxide ceramic component precursor and an oxide ceramic precursor component, or
 - ii) a non-oxide ceramic component precursor,
 - said bloating agent having a boiling point below the temperature of said bubble promoting medium and being at least moderately soluble in said sol precursor, said volatile liquid bloating agent being added to said sol precursor as droplets or microdroplets at a pressure in the range 39.2 kPa to 107.9 kPa.
- 40 8. A method according to claim 7 wherein said bloating agent has a boiling point in the range of 25 to 100°C at atmospheric pressure.
9. A method according to either of claims 7 and 8 wherein said bloating agent is selected from the group consisting of halocarbons, aldehydes, alcohols, ethers, ketones, and combinations thereof.
- 45 10. A method according to any of claims 7 to 9 wherein said bubble promoting medium is selected from the group consisting of esters of long chain fatty acids and derivatives thereof and long chain alcohols and combinations thereof.
- 50 11. A method according to any of claims 7 to 10 comprising the further step:

firing said green microbubbles to provide ceramic microbubbles as claimed in any of claims 1 to 5 comprising at least a non-oxide phase, said firing step optionally taking place in the presence of an agglomeration preventative agent.
- 55 12. A method according to claim 11 wherein a carbon-containing agglomeration preventative agent is used.



Al₂O₃ and TiN phases were present in the sample.

The zirconia gel bubbles produced in Example 4 were fired to 1480°C for 2 hours in N₂ and Ar atmospheres without aid of Solka-Floc or carbon black powder. The crystalline phases found by XRD analysis in the sample fired to 1480°C in an argon atmosphere were ZrC and monoclinic ZrO₂ and in the sample fired to 1480°C in nitrogen atmosphere were cubic zirconia, zirconium nitride, and monoclinic zirconia.

Claims

- 10 1. Free-flowing, discrete ceramic microbubbles consisting essentially of either 1) a non-oxide ceramic component and an oxide ceramic component, or 2) non-oxide ceramic, each microbubble having a fine microstructured ceramic wall and a single central cavity, said microbubbles having a diameter in the range of 1 to 300 micrometers and a wall thickness of less than 10 percent of the diameter of the microbubbles.
- 15 2. Microbubbles according to claim 1 wherein the ratio of said non-oxide ceramic component to said oxide ceramic component is in the range 95:5 to 5:95 parts by weight.
- 20 3. Microbubbles according to either of claims 1 and 2 wherein said ceramic comprises at least one of a metal nitride, a metal carbide, and a metal oxide.
4. Microbubbles according to any of claims 1 to 3 wherein said cavities are a vacuum or said cavities contain a gas.
- 25 5. Microbubbles according to any of claims 1 to 4 wherein said ceramic walls are selected from the group consisting of aluminum-, titanium-, zirconium-, and silicon-containing ceramics.
6. A shaped article comprising microbubbles according to any of claims 1 to 5.
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 - 35 i) a non-oxide ceramic component precursor and an oxide ceramic precursor component, or
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- 40 8. A method according to claim 7 wherein said bloating agent has a boiling point in the range of 25 to 100°C at atmospheric pressure.
9. A method according to either of claims 7 and 8 wherein said bloating agent is selected from the group consisting of halocarbons, aldehydes, alcohols, ethers, ketones, and combinations thereof.
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 - firing said green microbubbles to provide ceramic microbubbles as claimed in any of claims 1 to 5 comprising at least a non-oxide phase, said firing step optionally taking place in the presence of an agglomeration preventative agent.
- 55 12. A method according to claim 11 wherein a carbon-containing agglomeration preventative agent is used.



Patentansprüche

1. Rieselfähige, diskrete Keramikmikrobläschen, im wesentlichen bestehend entweder aus
 - 1) einer oxidfreien Keramikkomponente und einer Oxidkeramikkomponente oder
 - 2) oxidfreien Keramik, wobei jedes Mikrobläschen eine feine Keramikwand mit Mikrostruktur und einen einzelnen zentralen Hohlraum aufweist und die Mikrobläschen einen Durchmesser im Bereich von 1 bis 300 Mikrometer und eine Wandstärke von weniger als 10 % des Durchmessers der Mikrobläschen aufweisen.
2. Mikrobläschen nach Anspruch 1, bei welchen das Verhältnis der oxidfreien Keramikkomponente zu der Oxidkeramikkomponente im Bereich von 95:5 bis 5:95 Gewichtsteilen liegt.
3. Mikrobläschen nach einem der Ansprüche 1 und 2, bei welchen die Keramik mindestens ein Metallnitrid, ein Metallocarbid und ein Metalloxid umfaßt.
4. Mikrobläschen nach einem der Ansprüche 1 bis 3, bei welchen die Hohlräume ein Vakuum sind oder ein Gas enthalten.
5. Mikrobläschen nach einem der Ansprüche 1 bis 4, bei welchen die Keramikwände ausgewählt werden aus der Gruppe, bestehend aus Keramikwerkstoffen, die Aluminium, Titan, Zirkonium und Silicium enthalten.
6. Geformter Gegenstand, umfassend Mikrobläschen nach einem der Ansprüche 1 bis 5.
7. Verfahren zur Schaffung von grünen Mikrobläschen, umfassend die Schritte:
 - a) Zusetzen einer Mischung von Sol-Präkursor und einem flüchtigen flüssigen Blähmittel zu einem die Bläschenbildung fördernden Mittel bei einer Temperatur im Bereich von 50 ° bis 150 °C zum Schaffen von grünen, hohlen Mikrobläschen, wobei der Sol-Präkursor entweder
 - i) einen Präkursor einer oxidfreien Keramikkomponente und einen Präkursor einer Oxidkeramikkomponente umfaßt oder
 - ii) einen Präkursor einer oxidfreien Keramikkomponente, wobei das Blähmittel einen Siedepunkt unterhalb der Temperatur des Mittels zum Fördern der Bläschenbildung hat und mindestens in dem Sol-Präkursor mäßig löslich ist und das flüchtige, flüssige Blähmittel zu dem Sol-Präkursor in Form von Tröpfchen oder Mikrotröpfchen bei einem Druck im Bereich von 39,2 kPa bis 107,9 kPa zugesetzt wird.
8. Verfahren nach Anspruch 7, bei welchem das Blähmittel einen Siedepunkt im Bereich von 25 ° bis 100 °C bei Atmosphärendruck hat.
9. Verfahren nach einem der Ansprüche 7 und 8, bei welchem das Blähmittel ausgewählt wird aus der Gruppe, bestehend aus Halogenkohlenwasserstoffen, Aldehyden, Alkoholen, Ethern, Ketonen und deren Kombinationen.
10. Verfahren nach einem der Ansprüche 7 bis 9, bei welchem das Mittel zum Fördern der Bläschenbildung ausgewählt wird aus der Gruppe, bestehend aus Estern, langkettigen Fettsäuren und deren Derivaten und langkettigen Alkoholen und deren Kombinationen.
11. Verfahren nach einem der Ansprüche 7 bis 10, umfassend ferner den Schritt:
Brennen der grünen Mikrobläschen zum Schaffen von Keramikmikrobläschen entsprechend den Ansprüchen 1 bis 5, umfassend mindestens eine oxidfreie Phase, wobei der Schritt des Brennens wahlweise in Gegenwart eines Agglomerationsverhüters erfolgt.
12. Verfahren nach Anspruch 11, bei welchem ein Kohlenstoff enthaltender Agglomerationsverhüter verwendet wird.



Revendications

1. Microbulles céramiques discrètes, à écoulement libre, formées essentiellement 1) d'un composant de céramique non oxydée et d'un composant de céramique oxydée, ou 2) d'une céramique non oxydée, chaque microbulle ayant une paroi céramique fine à microstructure et une cavité centrale unique, lesdites microbulles ayant un diamètre compris entre 1 et 300 micromètres et une épaisseur de paroi de moins de 10 % du diamètre des microbulles.
2. Microbulles selon la revendication 1, dans lesquelles le rapport dudit composant de céramique non oxydée audit composant de céramique oxydée est compris entre 95:5 et 5:95 parties en poids.
3. Microbulles selon la revendication 1 ou 2, dans lesquelles ladite céramique comprend au moins un nitrure métallique, un carbure métallique ou un oxyde métallique.
4. Microbulles selon l'une quelconque des revendications 1 à 3, dans lesquelles lesdites cavités sont un vide, ou lesdites cavités contiennent un gaz.
5. Microbulles selon l'une quelconque des revendications 1 à 4, dans lesquelles lesdites parois céramiques sont choisies dans le groupe constitué des céramiques contenant de l'aluminium, du titane, du zirconium ou du silicium.
6. Article façonné comprenant des microbulles selon l'une quelconque des revendications 1 à 5.
7. Procédé de formation de microbulles crues, comprenant les étapes consistant à :
 - a) ajouter un mélange comprenant un précurseur de sol et un agent gonflant liquide volatil à un milieu favorisant la formation de bulles, à une température comprise entre 50 et 150 °C, pour former des microbulles creuses crues, ledit précurseur de sol comprenant :
 - i) un précurseur de composant de céramique non oxydée et un composant précurseur de céramique oxydée, ou
 - ii) un précurseur de composant de céramique non oxydée,
 ledit agent gonflant ayant un point d'ébullition situé au-dessous de la température dudit milieu favorisant la formation de bulles et étant au moins moyennement soluble dans ledit précurseur de sol, ledit agent gonflant liquide volatil étant ajouté audit précurseur de sol, sous la forme de gouttelettes ou de microgouttelettes, à une pression comprise entre 39,2 kPa et 107,9 kPa.
8. Procédé selon la revendication 7, selon lequel ledit agent gonflant a un point d'ébullition compris entre 25 et 100 °C à la pression atmosphérique.
9. Procédé selon la revendication 7 ou 8, selon lequel l'agent gonflant est choisi dans le groupe constitué d'hydrocarbures halogénés, d'aldéhydes, d'alcools, d'éthers, de cétones, et de combinaisons de ceux-ci.
10. Procédé selon l'une quelconque des revendications 7 à 9, selon lequel ledit milieu favorisant la formation de bulles est choisi dans le groupe constitué d'esters d'acides gras à chaîne longue et de dérivés de ceux-ci, et d'alcools à chaîne longue, et de combinaisons de ceux-ci.
11. Procédé selon l'une quelconque des revendications 7 à 10, comprenant l'étape supplémentaire consistant à :

calciner lesdites microbulles crues pour former des microbulles céramiques telles que revendiquées dans l'une quelconque des revendications 1 à 5, comprenant au moins une phase non oxydée, ladite étape de calcination se déroulant éventuellement en présence d'un agent empêchant l'agglomération.
12. Procédé selon la revendication 11, selon lequel on utilise un agent carboné empêchant l'agglomération.