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(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors: DUNMEAD, Stephen, D.; 4604 Autumn Ridge North, Midland, MI 48642 (US). WEIMER, Alan, W.; 3857 Old Pine Trail, Midland, MI 48642 (US). CARROLL, Daniel, F.; 701 Sylvan Lane, Midland, MI 48640 (US). EISMAN, Glenn, A.; 2101 Sylvan Lane, Midland, MI 48640 (US). COCHRAN, Gene, A.; 1201 Marriet Court, Midland, MI 48640 (US). SUSNITZKY, David, W.; 412 Hunters Ridge, Midland, MI 48640 (US). BEAMAN, Donald, R.; 930 Balfour Street, Midland, MI 48640 (US). NILSEN, Kevin, J.; 1032 Price Road, Midland, MI 48640 (US).

(74) Agent: SELBY, Robert, W.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).

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(57) Abstract

Prepare silicon nitride-silicon carbide composite powders by carbothermal reduction of crystalline silica powder, carbon powder and, optionally, crystalline silicon nitride powder. The crystalline silicon carbide portion of the composite powders has a mean number diameter less than about 700 nanometers and contains nitrogen. The composite powders may be used to prepare sintered ceramic bodies and self-reinforced silicon nitride ceramic bodies.

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SILICON NITRIDE/SILICON CARBIDE COMPOSITE POWDERS, THEIR PREPARATION AND DENSIFIED MATERIALS PREPARED USING THE COMPOSITE POWDERS

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The invention relates to synthesis of silicon nitride/silicon carbide (Si_3N_4/SiC) composite powders via carbothermal reduction of a mixture of silica (SiO_2) and carbon (C) powders, particularly to those composite powders wherein the silicon carbide portion contains an amount of nitrogen, and to resulting composite powders. The invention also relates to densified bodies, including self-reinforced silicon nitride (SRS) bodies, prepared from the composite powders, especially to those densified by pressureless sintering.

A known method of preparing Si_3N_4 powder is carbothermal synthesis, a reaction of nitrogen with SiO_2 powder contained in an admixture of SiO_2 and carbon (especially powdered carbon). Komeya et al. (U.S. Patent No. 4,428,916) prepare alpha-Si_3N_4 (α-Si_3N_4) powder in a nonoxidizing atmosphere by adding a seed such as Si_3N_4 powder, SiC powder or silicon oxynitride (SiON) powder, to the admixture. EP 206,795 teaches that addition of silicon (Si) metal increases α-Si_3N_4 yield. Inoue et al. (U.S. Patent No. 4,514,370) use a Si_3N_4 seed that is prepared by carbothermal synthesis at a temperature of 1350-1550° Centigrade (°C). DT 2,818,545 teaches that α-Si_3N_4 seed yields a product with a high α-Si_3N_4 content. JP 63-176,301 uses a Si_3N_4 seed having a beta-Si_3N_4 (β-Si_3N_4) content of 5-50 weight percent (wt%), based on seed weight, to prepare Si_3N_4 powder with a β-Si_3N_4 content of 1-20 wt%, based on powder weight. JP 80-015,946 discloses use of a carbohydrate, such as sucrose or starch, as a binder for mixed metal oxide powders and calcining the binder to form a carbonaceous residue. Niihara et al. (U.S. Patent No. 5,134,097) densify a physical mixture of Si_3N_4 and SiC powders to form a material having a matrix phase wherein SiC grains are located between and within Si_3N_4 grains and a disperse phase of SiC grains and SiC whiskers. Pyzik et al. (U.S. Patent Nos. 4,883,776; 4,919,689; 5,021,372; 5,091,347; 5,118,645; and 5,120,328) prepare SRS ceramic bodies from mixtures of Si_3N_4 powder and other powdered components that help densify the mixture (densification aids), convert α-Si_3N_4 to β-Si_3N_4 (conversion aids) and cause the β-Si_3N_4 to form elongated whiskers (whisker growth enhancing aids). Pyzik et al. require at least one of each aid.

A second method of preparing Si_3N_4 powder, known as direct nitridation, reacts silicon (Si) metal with nitrogen. The resulting powder may contain substantial impurity levels. Although hydrofluoric acid may be used to leach out at least some of these impurities, its use tends to lead to high residual fluorine contents.

A third method of preparing Si_3N_4 powder, known as diimide synthesis, reacts a halogenated silane compound and a nitrogen compound such as ammonia. The resulting powder has a residual chlorine content of at least 10 parts per million (ppm) of powder.

A first aspect of the invention is a process for preparing a silicon nitride-silicon carbide composite powder, the silicon carbide portion containing nitrogen, which comprises heating an admixture that comprises crystalline silica powder, carbon powder, and, optionally, crystalline silicon nitride powder to a temperature of from 1350°C to 1600°C in the presence of a nitrogen-containing atmosphere, preferably flowing, for a period of time sufficient to convert the admixture to a composite α-silicon nitride/silicon carbide powder, the silicon carbide portion of the powder having a mean number diameter within a range of from 10 to 700 nanometers and containing an amount of nitrogen, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion.

Mean number diameter (MND), also known as mean equivalent circular diameter, is a calculated value determined as described by John C. Russ, in Computer-Assisted Microscopy: The Measurement and Analysis of Images, at pages 182 and 192 (1990).

In a preferred variation of the first aspect, the admixture is, prior to heating to the temperature of from 1350°C to 1600°C, blended with a binder composition and formed into shaped masses of material that are then converted to calcined masses by heating them to a temperature sufficient to decompose components of the binder composition into a solid carbonaceous residue and maintaining that temperature until evolution of residual gases effectively ceases, the calcined masses having a carbon content that is greater than stoichiometrically required to reduce the silica via carbothermal reduction.

"Shaped masses of material", "shaped masses" and "masses" are used interchangeably to refer to a mass or body that has a shape suitable for processing as described herein. The shape is not particularly critical and may take on any solid geometric configuration such as spherical, ellipsoidal, cylindrical or conical. Commonly used terms for such shapes include, without limitation, "aggregates", "granules" and "pellets". As such, these terms may also be used interchangeably with masses and its equivalents.

A second aspect of the invention is a silicon nitride-silicon carbide composite powder comprising a silicon nitride phase that is at least 90 percent by weight, based upon phase weight, α-silicon nitride and a silicon carbide phase that is in the form of particles having a mean number diameter within a range of from 10 to 700 nanometers, the silicon carbide phase having a nitrogen content, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion, the silicon carbide phase being present in an amount of from greater than zero to 50, preferably from 0.01 to 25, more preferably from 0.1 to 15, still more preferably from 1 to 10 percent by weight, based upon composite powder weight, the composite powder having a BET surface area of

from 3 to 15 m^2/g. The second aspect also includes silicon nitride-silicon carbide composite powders wherein the silicon carbide phase is in the form of particles having a bimodal distribution, the bimodal distribution having a first distribution peak located at a mean number diameter within a range of from 10 to 200 nm and a second distribution peak located at a mean number diameter within a range of from 200 to 700 nm.

"BET surface area" refers to powder or particle surface area as measured by a conventional adsorption method such as that taught by S. Brunauer, P. H. Emmett and E. Teller in Journal of the American Chemical Society, volume 60, page 309 (1938).

A third aspect of the present invention is a process for preparing a self-reinforced silicon nitride ceramic body which comprises subjecting a powdered admixture of a carbothermally synthesized silicon nitride/silicon carbide composite powder, a densification aid, a conversion aid, at least one whisker growth enhancing aid and, optionally, a catalyst to conditions of temperature and pressure sufficient to yield a ceramic body having a density of at least 96 percent of theoretical density and form, in situ, β-silicon nitride whiskers having an average aspect ratio of at least 2.5, the body having both a granular and an intragranular distribution of residual silicon carbide grains and a fracture toughness of at least 7 $MPa \cdot m^{1/2}$, the intragranular silicon carbide grains having a mean number diameter within a range of from 10 to 400 nanometers, at least a portion of the intragranular silicon carbide grains containing nitrogen, as determined by parallel electron energy loss spectroscopy, in an amount that is within a range of from 2 to 10 percent by weight of the silicon carbide. The composite powder is preferably that of the second aspect of the invention.

A fourth aspect of the present invention is a self-reinforced silicon nitride/silicon carbide ceramic body having a density of at least 96 percent of theoretical density and comprising a crystalline phase of β-silicon nitride of which at least about 20 volume percent, as measured by viewing one plane of the body by scanning electron microscopy, is in the form of whiskers having an average aspect ratio of at least 2.5 and a glassy grain boundary phase in an amount not greater than 35 percent by weight of total body weight, the silicon carbide being distributed, with respect to the β-silicon nitride whiskers, as granular and intragranular submicrometer grains, the body having a fracture toughness of at least 7 $MPa \cdot m^{1/2}$, the intragranular silicon carbide grains having a mean number diameter within a range of from 10 to 400 nm, at least a portion of the intragranular silicon carbide grains containing nitrogen, as determined by parallel electron energy loss spectroscopy, in an amount that is within a range of from 2 to 10 percent by weight of the silicon carbide. The self-reinforced silicon nitride/silicon carbide ceramic body of this aspect is preferably prepared using the process of the the third aspect and the composite powder of the second aspect.

A fifth aspect of the present invention is a silicon nitride-silicon carbide composite powder having a silicon nitride phase and a silicon carbide phase, the silicon nitride phase having a phase purity of > 10% β-Si_3N_4 and comprising rod-like β-Si_3N_4 crystallites that have a

mean number diameter of about 0.04 μm, the number diameter ranging from 0.01 to 0.10 μm, and a mean aspect ratio of from 5/1 to 8/1, ranging from 1.5/1 to 21/1 and α-Si_3N_4 crystallites that have a mean number diameter of from 0.1 to 0.2 μm, the number diameter ranging from 0.03 to 0.5 μm.

The composite powders of the fifth aspect are prepared via a modification of the process of the first aspect of the present invention. The modification comprises using a seed Si_3N_4 that has a β-Si_3N_4 content in excess of 75 wt%.

Preparation of the composite α-silicon nitride/silicon carbide powder via carbothermal reduction is represented by an equation as follows:

$$3\,SiO_2 + (6+x)C + 2N_2 + y\,Si_3N_4 = (1+y)\,Si_3N_4 + 6\,CO + xC$$

wherein x is a real number within a range of from greater than 0 to 18 and y is a real number within a range of from 0 to 1.28. A stoichiometric amount of carbon (C) would require x to be 0. The real number for x is desirably from 0.6 to 12, preferably from 0.6 to 6. The real number for y is desirably from 0.05 to 1.1, preferably from 0.15 to 0.9, more preferably from 0.2 to 0.8, still more preferably from 0.26 to 0.77, and most preferably from 0.26 to 0.52.

Three terms may be used to describe the distribution of SiC grains relative to Si_3N_4 grains in sintered bodies containing both. "Granular" refers to SiC grains dispersed in glassy grain boundary pockets located at triple points between Si_3N_4 grains. "Intragranular" refers to SiC grains dispersed within Si_3N_4 grains. "Intergranular" refers to SiC grains disposed along grain boundaries between two adjacent Si_3N_4 grains.

Temperatures and temperature ranges disclosed herein are primarily intended as guidelines. With changes in measurement device, reactor or other apparatus, or location of temperature measurement, some variation is expected. A skilled artisan can readily determine appropriate adjustments of the temperatures or temperature ranges without undue experimentation.

As noted in the first aspect, an admixture suitable for use in preparing silicon nitride-silicon carbide composite materials contains crystalline silica powder, carbon powder and optionally, crystalline silicon nitride powder. Components of the admixture are also referred to as starting materials. Proper selection of carbon and silica sources for use as starting materials and seeding with fine Si_3N_4 crystallites allow control of the size of Si_3N_4 and SiC crystallites in resultant composite powders. The size of SiC crystallites depends, to some extent, on starting carbon crystallite size. With all other parameters being equal, as carbon crystallite size decreases so does composite powder SiC crystallite size. SiC crystallite size is largely unaffected by SiO_2 source or the presence or absence of seed. The size of Si_3N_4 crystallites depends heavily upon the presence of seed and the surface area and crystallinity of the starting SiO_2. The size of starting carbon powder has much less, if any, effect on the resulting Si_3N_4 crystallite size. A high purity composite powder with a SiC grain size (MND) less than about 100

nm, preferably less than about 50 nm, and a Si_3N_4 grain size (MND) of about 0.2 μm can be produced by reacting a seeded (0.2 seed/SiO_2 ratio and high purity α-phase Si_3N_4) acetylene carbon black/high purity quartz precursor.

Si_3N_4 crystallites tend to contain small pores described as "micropores". In addition to having an effect upon SiC crystallite size, the starting carbon crystallite size also has an effect upon micropore size. As a general rule, an increase in carbon crystallite size leads to a corresponding increase in micropore size.

Starting material (carbon and silica) purity has a measurable effect upon resultant composite powder purity. Each raw material or starting material has a purity that is desirably at least 96%, preferably at least 98.6, more preferably at least 98.9, still more preferably at least 99.5% and most preferably greater than or equal to 99.8%.

The silica is preferably provided by crystalline quartz that is at least 98.9, more preferably at least 99.5% and most preferably at least 99.8% pure. The quartz preferably has a surface area (S.A.) of greater than (>) 0.2 square meters per gram (m^2/g) and a mean particle size (d_{50}) by weight percent (wt%), as determined by laser light scattering using a model SPA MICROTRAC™ apparatus, of less than 15 micrometers (μm). If a different subscript, such as d_{10} is used in conjunction with a specified particle size, it means that 10 weight percent of the particles have a particle size less than or equal to the specified size. Silica mean particle size may be reduced by milling using a jet mill wherein the wear parts are fabricated from Si_3N_4, SiC or B_4C and other non-wearing parts are lined with urethane. The SiO_2 mean particle size (d_{50}) is more preferably less than about 10 μm.

The carbon powder used as a starting material has a surface area that is preferably at least 20 m^2/g, more preferably at least 25 m^2/g, and most preferably at least 70 m^2/g. Average particle sizes (MND) that correspond respectively to the surface areas are 0.10 μm, 0.06 μm and 0.03 μm.

Silica purity and morphology also affect whether the composite powder has β-Si_3N_4 whiskers or fibers protruding from α-Si_3N_4 crystallites. The protruding β-Si_3N_4 whiskers occur when the SiO_2 is either amorphous, without regard to purity, or crystalline, but relatively impure. A moderately sized (surface area of 1.9 m^2/g or greater), high purity (greater than 99.8%) crystalline quartz yields α-Si_3N_4 crystallites from which few, if any, β-Si_3N_4 whiskers or fibers protrude.

Although satisfactory silicon nitride-silicon carbide composite powders can be prepared from admixtures that lack crystalline silicon nitride, it is a preferred admixture component. The crystalline silicon nitride serves as a seed material.

One preferred seed material has an α-Si_3N_4 phase content of at least about 90 wt%, preferably at least 95 wt%, based upon Si_3N_4 weight, a SiC content of less than about 1.5 wt%, a SiO_2 content of less than about 10 wt%, the SiC and SiO_2 contents being based upon seed material weight, and a surface area of at least 7.5 m^2/g, preferably at least 10 m^2/g. The

SiC and SiO_2 contents are calculated based upon an assumption that all carbon in the composite powder is in the form of SiC and all oxygen in the composite powder is present as SiO_2. All subsequent references to SiC and SiO_2 content of a composite powder are based upon this assumption. Occasionally, however, other forms of carbon, such as graphite particles or carbon tubes, may be observed.

A second preferred seed material is a high purity α-Si_3N_4/SiC powder prepared by carbothermal synthesis, as described herein, and having a Si_3N_4 content of at least 95 wt%, and a combination of an amount of SiC and an amount of a SiO_2, each amount being greater than 0.0 wt%, that totals no more than 5 wt%, all percentages being based on powder weight. The seed also has: a surface area of from 3 to 15 m^2/g, desirably 7.5 m^2/g; a d_{10} of from 0.1 to 0.5 µm, desirably 0.38 µm; a d_{50} of less than 1 µm, desirably from 0.5 to 1 µm, and preferably 0.86 µm; and a d_{90} of from 1 to 4 µm, desirably 2.5 µm. The seed is desirably present in an amount sufficient to provide a ratio of seed/SiO_2 that falls within a range of from 0.05:1 to 1:1. The ratio is preferably from 0.1:1 to 0.6:1, more preferably from 0.15:1 to 0.4:1, and most preferably 0.2:1.

A third preferred silicon nitride seed material has a β-Si_3N_4 phase content of at least 75 wt%. The use of this seed material yields a Si_3N_4/SiC composite powder wherein the Si_3N_4 phase contains both α-Si_3N_4 and β-Si_3N_4, the β-Si_3N_4 being present in an amount of at least 10 wt%, based upon total Si_3N_4 content. The β-Si_3N_4 is in the form of rod-like β-Si_3N_4 crystallites that have a MND of about 0.04 µm, the number diameter ranging from 0.01 to 0.10 µm, and a mean aspect ratio of from 5/1 to 8/1, ranging from 1.5/1 to 21/1 and α-Si_3N_4 crystallites that have a MND of from 0.1 to 0.2 µm, the number diameter ranging from 0.03 to 0.5 µm.

The admixture may also include an amount of silicon metal powder. When used, the amount should be sufficient to provide a ratio of silicon metal powder to silicon dioxide powder that falls within a range of from 0.05:1 to 1:1. The range is preferably from 0.1:1 to 0.5:1.

The admixtures used to prepare the silicon nitride-silicon carbide composite powders may be heated to a reaction temperature as is. The admixtures are, however, preferably blended with a binder composition prior to heating to the reaction temperature.

The binder composition is desirably a product of a condensation reaction between at least one first reactant that has at least one reactive hydroxyl moiety and at least one second reactant having at least one reactive nitrogen-containing moiety. The first reactant is desirably selected from monosaccharides, disaccharides, polysaccharides, starches, modified starches, soy protein, cellulose ethers and cellulose ether derivatives. The second reactant is desirably an amine or an amide.

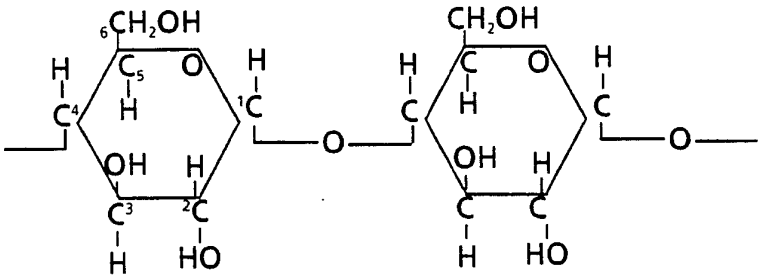
The first reactant is preferably selected from sucrose, fructose, glucose, mannose, xylose, raffinose, dextrin, amylose, maltose, lactose, arabinose, dextrose, galactose,

amylopectin, glucose polymers, xylose polymers, copolymers of glucose and xylose (gluco-xylans), invert sugar, partially invert sugar, molasses from sucrose refining, whey from milk processing, corn syrup, starch, modified starch, methylcellulose, ethylcellulose, hydroxypropyl-methylcellulose, hydroxyethylcellulose, sodium carboxymethylcellulose, carboxymethylcellulose and soy protein. The first reactant is more preferably at least one of corn starch, wheat starch, sucrose, fructose, soy protein, and cellulose ethers.

The second reactant is preferably selected from cyanoguanadine, melamine, urea, hexamethylene tetramine, trimethylamine, diethanolamine, triethanolamine, tetramethylene diamine, acetoguanamine, benzyldimethylamine, methylolmelamine, alkylated methylol-melamine, hexamethoxymethyl melamine, N,N'-dimethyl-p-phenylene diamine, tetraaminobenzene, diaminobenzidine, thiourea, formamide, acetamide, benzamide, oxamide, succinamide, malonamide, guanidine, biuret, triuret, dicyandiamide, biurea, ethylene urea, ammelide, ammeline, aminoguanidine, semicarbazide, thiosemicarbazide and acrylamide. The second reactant is more preferably melamine, hexamethylene tetramine, cyanoguanadine or urea.

The terms "starch" and "modified starch", as used herein, are defined in Condensed Chemical Dictionary, Eleventh Edition, Van Nostrand Reinhold Company, Inc.(1987), at pages 1089-90. The definitions are as follows:

--Starch (CAS: 9005-84-9), a carbohydrate polymer having the following repeating unit:



It is composed of about 25% amylose (anhydroglucopyranose units joined by glucosidic bonds) and 75% amylopectin, a branched-chain structure. Properties: White, amorphous, tasteless powder or granules; various crystalline forms may be obtained, including microcrystalline. Irreversible gel formation occurs in hot water; swelling of granules can be induced at room temperature with such compounds as formamide, formic acid, and strong bases and metallic salts. Occurrence: Starch is a reserve polysaccharide in plants (corn, potatoes, tapioca, rice, and wheat are commercial sources).

--Starch, modified. Any of several water-soluble polymers derived from a starch (corn, potato, tapioca) by acetylation, chlorination, acid hydrolysis, or enzymatic action. These reactions yield starch acetates, esters, and ethers in the form of stable and fluid solutions and films. Modified starches are used as textile sizing agents and paper coatings. Thin-boiling starches have high gel strength, oxidized starches made with sodium hypochlorite have low gelling tendency. Introduction of carboxyl, sulfonate, or sulfate groups into starch gives sodium or ammonium salts of anionic starches, yielding clear, non-gelling dispersions of high viscosity. Cationic starches result from addition of amino groups. The glucose units of starch can be crosslinked with such agents as formaldehyde, soluble metaphosphates, and epichlorohydrin.

The admixture of crystalline silica powder, carbon powder, and, optionally crystalline silicon nitride powder may, without any intermediate processing, be heated to a reaction temperature of from 1350°C to 1600°C in the presence of a nitrogen-containing atmosphere, preferably flowing, for a period of time sufficient to convert the admixture to a composite α-silicon nitride/silicon carbide powder. A preferred procedure includes intermediate processing steps prior to heating to the reaction temperature. In the preferred procedure, the admixture is added to a binder composition, mixed with water, preferably deionized water, and converted into a blended material using conventional apparatus such as a ball mill that is partially filled with suitable media, preferably SiO_2-based media. Other media may also be used provided the media does not react with the starting materials or adversely affect resulting powders or articles prepared from the powders. A milling time of from 30 minutes to 10 hours, preferably from 2 to 6 hours, yields a blended material suitable for further processing into shaped masses of material. Further processing also uses conventional apparatus, such as an extruder, to convert the blended material into moist shaped masses such as pellets. The pellets may be of any shape or configuration that does not interfere with further processing. A cylindrical shape provides satisfactory results.

The nitrogen-containing atmosphere may be established by gaseous nitrogen, gaseous ammonia, gaseous mixtures of nitrogen and ammonia, gaseous mixtures of nitrogen, ammonia or both with an inert or noble gas such as argon, or gaseous mixtures of nitrogen, ammonia or both with hydrogen and, optionally, an inert or noble gas. The presence of ammonia tends to increase the amount of silicon carbide formed in the composite powders. The nitrogen-containing atmosphere may be static or flowing, but is preferably flowing. If the atmosphere is static, it must have a volume sufficient to maintain carbon monoxide generated during carbothermal reduction at a level below that which slows down or terminates carbothermal reduction. A level of carbon monoxide of less than about 3 percent by volume, preferably less than about 1.5 percent by volume, based upon total atmosphere volume is believed to be satisfactory.

The moist shaped masses are desirably placed in a container such as a quartz boat. The container and its contents are then placed in an apparatus, such as a tube furnace, and heated, under flowing nitrogen, inert gas or air, preferably nitrogen, to a temperature and maintained at that temperature for a period of time sufficient to dry the pellets and allow a condensation reaction between the first and second reactants to occur. The time and temperature will vary somewhat depending upon size of the shaped masses, their moisture content, choice of binder composition components and relative amounts of all components of the shaped masses. When using, for example, a blend of wheat and corn starches as a first reactant and melamine as a second reactant to form wet pellets having a diameter of 1/4 inch (0.6 cm) and a length of 3/8 inch (1.0 cm), a temperature of 150° Centigrade (°C) and a time of two hours is sufficient. Longer times are generally needed with lower temperatures. Suitable times and temperatures for other reactants, pellet sizes and component ratios are readily determined without undue experimentation.

After the condensation reaction is substantially complete, the shaped masses are heated to a higher temperature and maintained at that temperature for a period of time sufficient to calcine the shaped masses. As used herein, "calcine" means that the shaped masses are heated under an inert atmosphere, such as that provided by nitrogen or an inert gas such as argon, at a temperature sufficient to decompose components of the binder composition into a carbonaceous residue and maintained at that temperature until evolution of residual gases effectively ceases (approaches a rate of evolution of 0 liters per minute) at that temperature. If desired, air can be substituted for inert gas at temperatures below that at which carbon will oxidize. Calcination temperatures typically range from 250°C to 1000°C, preferably from 300°C to 350°C. Continuing the foregoing example, the shaped masses are heated to a temperature of 330°C over a period of 30 minutes and maintained at that temperature for a period of two hours. The tube furnace and its contents are then cooled to ambient temperature to yield calcined masses suitable for reaction to provide the composite powders. As in the case of effecting the condensation reaction, suitable times and temperatures for other reactants, shaped mass sizes and component ratios are readily determined without undue experimentation.

The admixture or the calcined masses (where the preferred intermediate processing steps are used) is/are heated to a reaction temperature of from 1350°C to 1600°C in the presence of a flowing nitrogen-containing atmosphere. Using the calcined masses for purposes of illustration, the calcined masses may be added to a reactor and then heated to the reaction temperature (slow heating) or added directly to a preheated reactor (rapid heating). For slow heating, an aliquot of the calcined masses is suitably placed in a crucible adapted for mixing crucible contents that is then placed in a rotary reactor apparatus prior to heating to the reaction temperature. Other apparatus, such as a pusher furnace, may also be used. For rapid heating, the aliquot may be added to a preheated crucible through which a nitrogen-

containing gas flows. Rapid heating preferably occurs at a rate of greater than about 100°C/sec and is believed to generate high local concentrations of volatile silicon monoxide (SiO) gas. These concentrations are believed to favor nucleation of α-Si_3N_4 particles over growth of α-Si_3N_4 particles. Heating rates of less than 100°C/second, also known as "slow heating", are believed to favor particle growth over particle nucleation. The apparatus used for either rapid heating or slow heating is not particularly critical and a skilled artisan can scale up from the apparatus used in succeeding examples to batch or continuous apparatus capable of handling larger quantities of starting material admixtures or calcined masses without undue experimentation.

The foregoing process may be modified to produce a silicon nitride-silicon carbide composite powder wherein the silicon carbide portion is present as a bimodal distribution. The presence of the bimodal distribution may be detected by transmission electron microscopy. A suitable modification involves heating to two different reaction temperatures. A first reaction temperature, maintained for a first period of time, is from 1350°C to less than 1500°C. The first period of time is preferably from 120 to 470 minutes and the first temperature is preferably from 1425 to 1490°C. A second reaction temperature, maintained for a second period of time that is shorter than the first period of time, is at least 1500°C, but less than about 1600°C. The second period of time is from preferably 10 to 120 minutes, and the second temperature is preferably from 1500 to 1600°C. Skilled artisans recognize that a multimodal (greater than bimodal) distribution of the silicon carbide portion is attainable by further apportioning of reaction temperatures and allocating appropriate periods of time.

The bimodal distribution preferably has a first distribution peak and a second distribution peak as determined from transmission electron micrographs. The first distribution peak is preferably located at a MND within a range of from 10 to 200 nanometers (nm). The second distribution peak is preferably located at a MND within a range of from 200 to 700 nm.

A second modification of the process provides for early preparation of at least some silicon carbide. The second modification, like the modification to generate a bimodal distribution of the silicon carbide portion, involves use of more than one reaction temperature. In this modification, heating proceeds to an initial temperature that thermodynamically favors formation of silicon carbide over formation of silicon nitride for a first period of time to generate submicrometer SiC crystallites. The initial temperature and the first period of time are sufficient to provide the composite powder with a silicon carbide content that is greater than 0 wt%, but less than about 50 wt%, based upon composite powder weight. The silicon carbide is in the form of crystallites having a MND that ranges from 10 nm to 700 nm. The initial temperature is preferably within a range of 1500-1550°C and the first period of time is from 1 minute to 45 minutes. Heating then proceeds at a second temperature that favors formation of Si_3N_4 over SiC for a second period of time that is longer than the first period of

time. The second temperature is within a range of from 1350°C to less than 1500°C and the second period of time is from 375 minutes to 419 minutes.

Modification of the process is not limited to manipulation of the reaction temperature. The silicon nitride-silicon carbide composite powder may be subjected to post synthesis procedures. One such procedure heats the composite powder to a temperature within a range of from 500°C to 1000°C in an oxidizing atmosphere for a period of time sufficient to effect removal of excess free carbon. The oxidizing atmosphere is established by any gas that will oxidize free carbon into a gaseous phase such as carbon monoxide or hydrogen cyanide at that temperature. The gas is suitably air, mixtures of air and nitrogen, ammonia, carbon dioxide, mixtures of carbon dioxide and carbon monoxide, hydrogen, mixtures of hydrogen and a hydrocarbon, or other oxidizing atmospheres known to those skilled in the art. The period of time is within a range of from 10 minutes to 6 hours. After removal of excess free carbon, the composite powder has a silicon nitride phase that is at least 90 percent by weight, based upon silicon nitride phase weight, α-silicon nitride and a silicon carbide phase. The silicon carbide phase is in the form of particles having a MND within a range of from 10 to 700 nanometers. The silicon carbide phase is present in an amount of from greater than 0 to 50 percent by weight, based upon composite powder weight, the composite powder having a BET surface area of from 3 to 15 m^2/g. The silicon carbide phase has a nitrogen content, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion

A second procedure, which may be used in place of, or subsequent to, the procedure to remove excess carbon subjects the composite powder to a heat treatment in the presence of nitrogen or an inert gas such as argon (or mixtures thereof), preferably flowing, at a temperature within a range of from 1400°C to 1500°C in a nonoxidizing atmosphere for a period of time sufficient to cause at least a portion of residual silicon dioxide to react with at least a portion of the silicon carbide. The heat treatment yields a composite powder with an increased silicon nitride content relative to the composite powder prior to the heat treatment. The period of time falls within a range that is desirably from more than five minutes to at least 24 hours, preferably from 4 hours to 12 hours.

The composite powders may be subjected to additional post synthesis processing after the heat treatment. The additional processing may include washing, leaching, grinding or a combination thereof. In some cases, it may be advantageous to wash the composite powder with water, an aqueous solution or a nonaqueous solution. Washing removes some excess carbon while improving handling characteristics of the composite powders by removing or reducing static charge associated with composite powder surfaces. Washing may be accomplished by placing the composite powder in a bath of a liquid medium such as water. With mild mechanical agitation, ultrasonic mixing or both, at least a portion of excess carbon separates from the composite powder and floats to the bath's upper surface. The excess carbon

is removed from the upper surface before the composite powder is recovered and dried. In other cases, it may be advantageous to use starting materials that contain metallic impurities. Advantages may stem from economic considerations or a desire to control final product characteristics. Leaching, or removal of metallic impurities, may be accomplished by treating the heat treated powder with any of a variety of acids such as hydrochloric acid, hydrofluoric acid or nitric acid. Hydrofluoric acid also removes at least a portion of residual SiO_2 in the product. A grinding or milling step may be used to control particle size and particle size distribution of the composite powders. Conventional apparatuses, such as an attritor or a ball mill, may be used for grinding. The composite powders may be used as a seed for subsequent synthesis of composite powders. If used as a seed, they may be used as synthesized or subsequent to milling.

Composite powders prepared with high purity starting materials and a high purity α-Si_3N_4 seed also have high purity: an α-Si_3N_4 phase purity of at least 95%; a Si_3N_4 crystallite MND of less than 0.3 µm; a surface area that lies within a range of from 8 to 13 m^2/g; a SiC content within a range of from greater than 0 to 50, preferably from 0.01 to 25, more preferably from 0.1 to 15, still more preferably from 1 to 10 wt%, based upon powder weight; and a SiC crystallite MND within a range of from 10 to 700 nm, desirably from 10 to 400 nm, and preferably less than 100 nm, more preferably less than 50 nm. At least a portion of the SiC crystallites have a nitrogen content of from 2 to 10 wt%, based upon SiC weight. The Si_3N_4/SiC composite also has: less than 2 wt% residual oxygen as monatomic O; and residual elemental impurities of less than 100 ppm calcium (Ca), less than 50 ppm iron (Fe), less than 200 ppm (preferably less than 50 ppm) aluminum (Al), less than 20 ppm sulfur (S), less than 50 ppm (preferably less than 10 ppm) fluorine (F), less than 10 ppm potassium (K) and less than 10 ppm chlorine (Cl). In addition, the α-Si_3N_4 crystallites are substantially free of protruding β-Si_3N_4 fibers.

The size and quantity of α-Si_3N_4 crystallites included as a seed in a starting powder mixture affect the size of α-Si_3N_4 crystallites in a product. Specifically, α-Si_3N_4 crystallites with a MND of less than 0.3 µm are prepared by reacting a precursor containing seed α-Si_3N_4 crystallites that have a MND of less than 0.2 µm and are present in an amount sufficient to establish a precursor seed/SiO_2 ratio of at least 0.15:1.

Composite powder composition and purity lead, in turn, to densified parts prepared therefrom with properties such as fracture toughness, strength and Weibull modulus that are increased over those obtained with lower purity powders or with powders that contain only Si_3N_4. The property improvements should occur regardless of the method used in preparing such parts.

A unique rod-like β-Si_3N_4 morphology results from a change in the seed material from a high (greater than 90 wt%) α-phase Si_3N_4 powder to a high (greater than 75 wt%) β-phase Si_3N_4 powder. The use of the latter powder as a seed yields a Si_3N_4/SiC composite

powder wherein the Si_3N_4 phase comprises both α-Si_3N_4 and β-Si_3N_4, the β-Si_3N_4 being present in an amount > 10 wt%, based upon total Si_3N_4 content. The β-Si_3N_4 comprises rod-like β-Si_3N_4 crystallites that have a MND of about 0.04 μm, the number diameter ranging from 0.01 to 0.10 μm, and a mean aspect ratio of from 5/1 to 8/1, ranging from 1.5/1 to 21/1 and α-Si_3N_4 crystallites that have a MND of from 0.1 to 0.2 μm, the number diameter ranging from 0.03 to 0.5 μm.

"Powder sinterability" is a relative measure of time required to attain a desired density such as 97 percent of theoretical density. A first powder is termed more sinterable than a second powder if the first powder can be sintered to the desired density in a shorter time, under identical sintering conditions and seed/silica ratios, than the second powder. Composite powders wherein the Si_3N_4 phase comprises both α-Si_3N_4 and β-Si_3N_4, the β-Si_3N_4 being in the form of rod-like crystallites, are more sinterable than composite powders prepared with a high α-phase Si_3N_4 seed and lacking the rod-like β-Si_3N_4 crystallites. The choice of binder, where used, also has an effect upon powder sinterability. As an illustration, a sucrose-based binder generally yields a more sinterable composite powder than an equivalent amount of a starch-based binder.

Addition of an amount of silicon (Si) metal powder to a starting material composition provides a measure of control over SiC content of the composite powder without adversely affecting size of the Si_3N_4 component, especially the α-Si_3N_4 component, of the composite powder. The starting material composition typically includes SiO_2, carbon powder, a seed material such as Si_3N_4 powder, and a binder. A ratio of Si metal weight to total starting material composition weight is desirably from 0.01:1 to 1:1, preferably from 0.1:1 to 0.5:1.

Rapid heating is one means of generating, in situ, fine SiC crystallites that serve as seeds for synthesis of α-Si_3N_4 crystallites. The SiC crystallites have a MND that ranges from 10 nm to 700 nm, preferably from 30 nm to 100 nm. A particularly suitable MND is 50 nm. The SiC crystallites, particularly the fine crystallites, result, at least in part, from initial, rapid heating of starting material compositions to temperatures that thermodynamically favor formation of SiC over formation of Si_3N_4. Temperatures within a range of 1500-1550°C provide acceptable results. Skilled artisans recognize that some SiC also forms at temperatures of less than 1500°C. The initial heating is of short duration, suitably from 1 minute to 45 minutes, desirably from 5 minutes to 30 minutes, preferably from 5 to 20 minutes. After the initial heating, the temperature is preferably reduced to a level that favors formation of Si_3N_4 over SiC. These times and temperatures are suitable for preparation of composite powders having SiC contents of no more than about 25 wt%, based upon composite powder weight. If greater SiC contents are desired, a higher initial temperature, a longer time at the initial temperature, or both should provide satisfactory results.

A measure of control over composite powder surface area can be gained by varying excess carbon content, seed content or both in the shaped and calcined masses of

starting materials (pellets). These parameters affect rates of nucleation and rates of growth of Si_3N_4 particles. An increase in excess carbon or a decrease in seed content, as reflected by a ratio of seed to SiO_2 in the calcined pellets, leads to an increase in composite powder surface area. A decrease in excess carbon or an increase in seed content, as reflected by the ratio of seed to silica in the calcined pellets, leads to a decrease in composite powder surface area. Therefore, a desired composite powder surface area can be attained by adjusting excess carbon content, seed/silica ratio or, preferably, both.

Post synthesis heat treatment of composite powders may be used to alter powder SiC and SiO_2 contents. It is believed, without intending to be bound thereby, that at least a portion of residual SiC reacts with at least a portion of residual SiO_2 during heating in the presence of nitrogen or an inert gas such as argon (or mixtures thereof), preferably flowing, at a temperature of from 1400°C to 1500°C for a period of time that ranges from less than 4 hours to more than 12 hours. A heat treatment time of as few as 5 minutes produces negligible changes in residual SiC and SiO_2 contents and may be uneconomical. Times in excess of 12 hours, such as 24 hours or more, while usable, provide diminishing economic returns. Suitable times will vary depending upon the heat treatment temperature as well as upon other variables such as amount of SiC and SiO_2 as well as particle size. By way of illustration, heat treatment of a composite powder having a residual SiO_2 content of 4.4 wt% and a residual SiC content of 1.5 wt% for 12 hours at 1500°C yields a residual SiO_2 content of 2.03 wt% and a residual SiC content of 0.9 wt% whereas a heat treatment of the same powder for 4 hours at 1400°C yields a residual SiO_2 content of 3.4 wt% and a residual SiC content of 1.4 wt%. The heat treatment also decreases internal porosity of powder particles and causes the particles to take on a more spherical shape. The decrease in porosity is accompanied by a concurrent decrease in powder surface area and leads to a solid or near solid crystallite structure.

The composite powders of the present invention are suitable for use in preparing SRS ceramic bodies. SRS ceramic bodies are formed at elevated temperatures, either with applied pressure, as in hot pressing, or with little or no applied pressure, as in low pressure gas sintering or pressureless sintering. The composite powders are combined with suitable densification aids, conversion aids, whisker growth enhancing compounds and, optionally, preformed reinforcing materials. U.S. Patent Number 5,021,372 defines densification aids (column 5, lines 49-61), conversion aids (column 6, lines 19-27) and whisker growth enhancing compounds (column 7, lines 4-18). U.S. Patent Number 5,021,372 also includes suitable compounds and amounts for such densification aids (column 5, line 62 through column 6, line 18), conversion aids (column 6, lines 35-55) and whisker growth enhancing compounds (column 7, line 19 through column 8, line 52). These teachings and those of related U.S. Patent Numbers 5,091,347; 5,098,449; 5,120,328; 5,118,645; 5,120,328; and 5,160,508 that discuss one or more of densification aids, conversion aids, whisker growth enhancing compounds and preformed reinforcing materials are incorporated herein by reference.

A densification aid is a compound that forms a liquid phase into which α-Si_3N_4 dissolves and in which mass transport rates of the silicon and nitrogen are quite rapid. The temperature at which the liquid phase forms varies with the densification aid. A conversion aid is a compound that forms a glassy phase through which mass transport is, in general, considerably slower than in the densification aid. Thus, α-Si_3N_4 dissolves in the conversion aid on heating, but is not readily densified. Notwithstanding this lack of densification, the conversion aid promotes rapid, essentially complete conversion of α-Si_3N_4 to β-Si_3N_4. Whisker growth enhancing compounds promote formation of β-Si_3N_4 whiskers.

A self-reinforced silicon nitride/silicon carbide ceramic body is desirably prepared by subjecting a powdered admixture of the silicon nitride/silicon carbide composite powder (prepared as described herein), a densification aid, a conversion aid, at least one whisker growth enhancing aid and, optionally, a catalyst to conditions of temperature and pressure sufficient to yield a ceramic body having a density of at least 96 percent of theoretical density and form, in situ, β-silicon nitride whiskers having an average aspect ratio of at least 2.5. The body has both a granular and an intragranular distribution of residual silicon carbide grains and a fracture toughness of at least 7 MPa·$m^{1/2}$. The intragranular silicon carbide grains have a MND within a range of from 10 to 400 nanometers. At least a portion of the intragranular silicon carbide grains contain nitrogen, as determined by parallel electron energy loss spectroscopy, in an amount that is within a range of from 2 to 10 percent by weight of the silicon carbide. If desired, the powdered admixture may be converted to a shaped body prior to being subjected to the conditions of temperature and pressure. The resulting ceramic body has a creep resistance that is greater than that obtained by substituting silicon nitride for the silicon nitride/silicon carbide composite powder. The resulting body includes a crystalline phase of β-silicon nitride of which at least about 20 volume percent, as measured by viewing one plane of the body by scanning electron microscopy, is in the form of whiskers having an average aspect ratio of at least 2.5 and a glassy grain boundary phase in an amount not greater than 35 percent by weight of total body weight. By using the silicon nitride/silicon carbide composite powders as the starting material, the resulting ceramic body also contains silicon carbide in an amount that is within a range of from greater than 0 percent by weight to 50 percent by weight, based upon combined weight of silicon nitride and silicon carbide.

The following examples are solely for purposes of illustration. They do not limit, either explicitly or implicitly, the scope of the present invention.

Example 1

Prepare a raw material feed mixture by mixing 41.7 parts by weight (pbw) SiO_2 (a high purity crystalline quartz having an average particle size < 10 µm), 33.3 pbw acetylene carbon black (commercially available from Chevron Chemical Company under the trade designation SHAWINIGAN BLACK™), and 25.0 pbw Si_3N_4 (UBE Industries, Limited under the trade designation SN E-10) in a ball mill half filled with a SiO_2-based media for five hours.

Transfer the raw material feed mixture to a blender, add 8.2 pbw wheat starch, 3.5 pbw corn starch and 5.9 pbw melamine, all parts being based on 100 parts by weight of raw material feed mixture, and blend for 20 minutes. Add sufficient water to yield a consistency suitable for extrusion and blend for an additional 20 minutes. Using an extruder equipped with a cutter, convert the blended mixture to moist shaped masses in the form of pellets having a diameter of about 0.25 inch (0.6 cm) and a length of about 0.38 inch (1 cm). Heat treat the moist pellets in nitrogen for 8 hours at 150°C, increase the heat to 330°C over a period of 1 hour and maintain that temperature for an additional 7 hours before allowing the pellets to cool naturally to ambient temperature (about 25°C). The pellets have a Si_3N_4 seed/SiO_2 ratio of 0.6:1.

Place 500 grams (g) of the heat treated pellets into a graphite crucible having a diameter of 9 inches (about 23 cm) and a depth of 9 inches (about 23 cm) and being inclined at an angle of 22.5 degrees with respect to horizontal. Six graphite lifts are attached to the inside of the crucible to aid in the mixing and turnover of the pellets. Place the crucible in the center of a radio frequency (RF) induction coil and attach it to a molybdenum shaft by which the crucible can be rotated. Rotate the crucible at 3 revolutions per minute (rpm) while inductively heating the crucible contents. Heat at 30°C/minute to 1500°C (as measured by a W-Re thermocouple in the center of the crucible) in the presence of nitrogen flowing at a rate of 40 standard liters per minute (slpm), hold at that temperature for 180 minutes and then allow the crucible contents to cool naturally to ambient temperature. Analysis of the pellets after cooling reveals an oxygen content of 1.19 weight percent (wt%) and a carbon content of 27.5 wt%. Remove excess carbon by heating the resultant pellets to a temperature of 700°C and maintaining that temperature for 3 hours while flowing a 50/50 air/nitrogen mix through the pellets at a rate of 20 slpm. After carbon removal is complete, allow the pellets to cool to ambient temperature and then convert the pellets to powder. The powder has a carbon content of 0.71 wt% (2.37 wt% as SiC) and an oxygen content of 2.11 wt%, all percentages being based upon powder weight. Transmission electron microscopy (TEM) shows that the carbon is in the form of nanosized SiC particles having a diameter ranging from 10 to 70 nm (0.01 to 0.07 μm).

Examples 2-5

Repeat Example 1, but vary the reaction temperature and time at that temperature as shown in Table I. Table I also shows the carbon content, equivalent SiC content, oxygen content and BET surface area of the powder after excess carbon removal (burnout). Table I includes comparable data for Example 1. Each powder has an α-Si_3N_4 content in excess of 95 wt% with SiC being in the form of nanometer-sized (nanosized) particles.

Table I

Example No.	Seed: SiO2 Ratio	Reaction Temp. (°C)	Reaction Time (min)	Product Powder Properties			
				Carbon Content (wt%)	SiC Content (wt%)	Oxygen Content (wt%)	Surface Area (m2/g)
1	0.6:1	1500	180	0.71	2.37	2.11	--
2	0.6:1	1450	400	0.29	0.97	1.78	8.0
3	0.6:1	1475	300	0.48	1.60	1.81	8.5
4	0.6:1	1525	300	3.99	13.30	2.95	8.5
5	0.2:1	1475	390	0.53	1.77	1.94	11.6

-- means not measured

The data in Table I show that reaction temperature and time at temperature have an effect upon carbon and oxygen contents of the powder. In addition, a comparison of Examples 3 and 5 shows that the seed:SiO_2 ratio affects the powder surface area.

Examples 6-10

Repeat Example 1, but vary the reaction temperature as shown in Table II and increase the time at reaction temperature to 390 minutes. Table II also shows the SiC content and size after carbon burnout.

Table II

Example Number	Temperature (°C)	SiC Content (wt%)	SiC MND (nm)
6	1450	1.33	35
7	1460	1.67	60
8	1475	4.67	140
9	1485	9.33	230
10	1500	48.09	310

The data in Table II show that reaction temperature has a marked effect upon both SiC content and size. The data suggest that a powder with a desired SiC content and size can, without undue experimentation, be prepared by selecting a combination of reaction parameters. Similar results and trends are expected with other raw material compositions that are disclosed herein as well as other times at reaction temperature.

Example 11

Repeat Example 3, but increase the time at reaction temperature to 390 minutes. In line with the formula $3\,SiO_2 + (6 + x)C + 2\,N_2 + y\,Si_3N_4 = (1 + y)\,Si_3N_4 + 6\,CO + x\,C$, $y = 0.77$ and $x = 6$ for this mixture. The pellets have a Si_3N_4 seed/SiO_2 ratio of 0.6:1. After carbon removal or burnout, the powder has a carbon content of 0.30 wt% (1.0 wt% as SiC) and an oxygen content of 1.78 wt%. As in Example 1, the powder has an α-Si_3N_4 phase content in excess of 95 wt% and contains nanosized SiC particles having a diameter ranging from 10 to 70 nm. The powder has a BET surface area of 8.0 m^2/g.

Examples 12-15

Repeat Example 11, but change the amounts of SiO_2, C and Si_3N_4 and the value for y as shown in Table III. Table III also includes powder properties of the powders after carbon burnout for Examples 11-15. As in Example 11, all powders have an α-Si_3N_4 phase content in excess of 95 wt% and contain nanosized SiC particles (10 to 70 nm).

Table III

Example No.	Raw Material Amounts (pbw)			y =	Product Powder Properties		
	SiO_2	C	Si_3N_4		C (wt%)	O (wt%)	S.A.* (m^2/g)
11	41.7	33.3	25.0	0.77	0.30	1.78	8.0
12	45.5	36.4	18.1	0.51	0.46	2.49	9.5
13	49.9	40.0	10.1	0.26	0.53	1.94	11.6
14	52.6	42.1	5.3	0.13	0.46	2.22	12.0
15	55.6	44.4	0.0	0	0.5	2.38	13.0

* means BET Surface Area

The data in Table III show that surface area (S.A.) increases as the seed to SiO_2 ratio decreases. The material with no seed (Example 15) has a higher S.A. than the other materials, but scanning electron microscopy (SEM) analysis shows that it has a blocky particle morphology. The blocky morphology leads to problems when the material is to be sintered. A material with a high S.A. and an equiaxed morphology is much more desirable than the blocky material from an ease of sintering point of view. At least a portion of the relatively high surface area for Example 15 is due to internal porosity. The material is, however, quite suitable for sintering if it is ground prior to sintering.

Example 16

Prepare three composite powder batches by replicating Example 11 save for changing the value for y as shown in Table IV. Prepare a fourth composite powder batch by duplicating Example 11 save for reducing the temperature to 1450°C. The carbon content, oxygen content and surface area for each powder are also shown in Table IV.

Convert a portion of each composite powder batch into a pressureless sinterable composition in accordance with the following recipe: 86.64 wt% composite powder, 6.26 wt% Y_2O_3, 2.85 wt% Al_2O_3 and 4.25 wt% total SiO_2. As used herein, "total SiO_2" refers to a combination of SiO_2 contained in the composite powder and added SiO_2. Attrit the composition for one hour in water using Si_3N_4 milling media. Use a roto-evaporator to dry the attrited combination into a formulated, sinterable powder. Convert the powder into test pieces by uniaxially pressing at 2500 pounds per square inch (psi) (17 MPa) then isostatically pressing at 40,000 psi (276 MPa). Pressureless sinter the test pieces at 1750°C for either 3 hours or 9 hours (Table IV) in a boron nitride crucible in a nitrogen atmosphere. The pressureless sintering procedure is taught in U.S. 5,120,328, particularly at column 8, line 3 through column

10, line 56. The relevant teachings of U.S. 5,120,328 are incorporated herein by reference. Table IV shows resulting densities in terms of percent of theoretical density.

Table IV

y =	Powder Properties			Sintered Body (% of Theoretical Density)	
	Carbon Content (wt%)	Oxygen Content (wt%)	Surface Area (m^2/g)	3 Hours at 1750°C	9 Hours at 1750°C
0.0	0.72	2.50	13	78.6	76.3
0.26	0.50	2.47	11	94.6	98.1
0.52	0.52	2.46	9	94.4	98.2
0.77	0.29	1.78	8	92.0	98.6

The data in Table IV demonstrate that use of a level of seed that is intermediate between no seed (y = 0.0) and more seed than needed to prepare sinterable composite powders (y is at least 0.77) is desirable when such powders are to be consolidated via pressureless sintering. As shown in Table IV, y values of 0.26 and 0.52 yield powders that are more sinterable than a y value of either 0.0 or 0.77 for a sintering time of 3 hours and a sintering temperature of 1750°C. There are no sharp demarcations at 0.26 and 0.52. As such, y values of less than 0.26, but greater than 0.0, or greater than 0.52, but less than 0.77 should provide satisfactory results. In fact, y values in excess of 0.77 may be acceptable if one is willing to accept longer sintering times. Similar results are expected under other pressureless sintering conditions, albeit with broader or narrower y value ranges. In any event, the presence of seed during powder synthesis yields powders that are more sinterable than those prepared in the absence of a seed.

Example 17

Repeat Example 16, but change the recipe, use ethanol rather than water during attrition, a graphite crucible rather than a boron nitride crucible and a powder bed of the same composition as the recipe, and increase the sintering time to 12 hours. The recipe is: 92.77 wt% of the Si_3N_4 composite powder of Example 1, 1.25 wt% Y_2O_3, 1.45 wt% MgO, 3.85 wt% SiO_2, 0.50 wt% ZrO_2 and 0.18 wt% Ta_2O_5. The resultant sintered part has a density of 99.5 percent of theoretical density.

Analyzing the sintered part via TEM shows that SiC is present and dispersed throughout the part (both intragranular and granular). There are no intergranular SiC particles. The intragranular SiC has a MND of 110 ± 70 nm and the granular SiC has a MND of

140 ± 40 nm. As such, the granular and intragranular SiC particles appear to be equivalent in size.

This example shows that the composite powder of the present invention can be used to prepare SRS materials with nanosize SiC-reinforced Si_3N_4 composite structures without a need to physically mix SiC materials into a sinterable composition.

Example 18

Repeat Example 1, but substitute 11.7 pbw of sucrose for the 8.2 pbw wheat starch and 3.5 pbw corn starch used in that example, reduce the reaction temperature from 1500°C to 1475°C, increase the time at temperature from 180 minutes to 390 minutes, and increase the carbon burnout temperature from 700°C to 800°C. The powder has a carbon content of 0.52 wt% and an oxygen content of 2.06 wt%, all percentages being based upon powder weight. The powder carbon content equates to a SiC content of 1.73 wt% that, by TEM, is in the form of nanosized SiC particles (diameter ranging from 10 to 70 nm). The powder has a BET surface area of 12.2 m^2/g. If the combination of starches used in Example 1 is substituted for sucrose, the product powder has an oxygen content of 1.78 wt%, a carbon content of 0.30 wt% and a BET surface area of 8.0 m^2/g.

This example demonstrates that product surface area can be varied based upon the binder used to prepare the heat treated pellets.

Example 19

Repeat Example 16, but use a different recipe and sintering times of 3 and 12 hours rather than 3 and 9 hours to prepare sintered bodies using composite powders from Examples 1 and 18. The recipe is: 91.90 wt% composite powder; 1.97 wt% Y_2O_3, 0.93 wt% MgO; 4.43 wt% total SiO_2; 0.56 wt% ZrO_2 and 0.21 wt% Ta_2O_5. Table V shows the composite powder source, binder type, composite powder surface area and percent theoretical density under the given sintering conditions.

Table V

Powder Source Example No.	Binder	Powder Surface Area (m2/g)	Sintered Body % Theoretical Density	
			1750°C 3 Hours	1750°C 12 Hours
1	Starch	8.0	90.0	98.8
18	Sucrose	12.2	94.1	98.9

The data in Table V demonstrate that the choice of binder used to prepare composite powders can have an effect upon powder sinterability. Powders that can attain a

higher density in a shorter time are believed to be more desirable than those that cannot attain such a density or require longer sintering times or higher sintering temperatures or both to attain an equivalent density. As such, those that are prepared with a sucrose-based binder are more sinterable than those prepared with a starch-based binder.

Example 20

Repeat Example 14, but modify the procedure by heating to a first temperature of 1475°C, holding at that temperature for a period of 360 minutes, then heating to a temperature of 1520°C at a rate of 5°C/min and holding at that temperature for 30 minutes before cooling. The resultant powder has a carbon content of 1.42 wt% (4.74 wt% as SiC) and an oxygen content of 2.42 wt%, all percentages being based upon powder weight. TEM shows that the carbon is in the form of SiC particles having a bimodal size distribution with distribution peaks located at MND's 0.12 ± 0.03 μm and at 0.44 ± 0.10 μm. Duplicating this procedure save for omitting the increase in temperature to above 1500°C yields a monomodal distribution of SiC particle sizes.

This example shows that modifications of SiC particle size distribution are possible via manipulation of combinations of reaction temperature and reaction time.

Example 21

Use the procedure and raw materials of Example 1, but reduce the amounts of wheat and corn starches respectively to 7.8 pbw and 3 pbw, to convert a raw material feed mixture of 47.2 pbw SiO_2, 37.8 pbw acetylene carbon black, 9.4 pbw Si_3N_4 and 5.6 pbw melamine into a product powder. The SiO_2 is a high purity quartz (Unimin Corp., Iota Standard) that has, in part, a Fe content of 5 ppm, an Al content of less than 50 ppm and a Ca content of less than 5 ppm. The product powder has a surface area of 10.1 m^2/g, a carbon content of 0.40 wt%, an oxygen content of 2.44 wt%, a Fe content of 31 ppm, an Al content of less than 50 ppm and a Ca content of 71 ppm, all parts and percentages being based upon powder weight. After milling using a jet mill wherein the wear parts are fabricated from Si_3N_4, SiC or B_4C and other non-wearing parts are lined with urethane, the SiO_2 has an average particle size of less than 10 μm.

Repeat Example 17 for a combination of 91.89 wt% of the product powder, 1.97 wt% Y_2O_3, 0.94 wt% MgO, 4.43 wt% total SiO_2, 0.56 wt% ZrO_2 and 0.21 wt% Ta_2O_5. The resultant sintered part has a density of 96.5 percent of theoretical density, a room temperature strength of 795 megapascals (MPa), a fracture toughness of 7.3 $MPa \cdot m^{1/2}$ and a Weibull modulus of 18. Jet milling the heat treated pellets after completing carbon removal yields a powder with a surface area of 10.4 m^2/g, a carbon content of 0.41 wt%, an oxygen content of 2.4 wt%, a Fe content of 17 ppm, an Al content of less than 50 ppm and a Ca content of 67 ppm. The sintered part has a density of 96 % of theoretical density, a room temperature strength of 750 MPa, a fracture toughness of 7.3 $MPa \cdot m^{1/2}$ and a Weibull modulus of 15. If a lower purity quartz, such as Silica B (Table XII), is substituted for the high purity crystalline quartz, the

product powder has correspondingly higher impurity levels. This powder converts to a sintered part having properties, such as room temperature strength and Weibull modulus, that are lower than those noted in this Example 21.

The foregoing results demonstrate that using high purity starting materials leads to Si_3N_4 powder with greater purity than when using lower purity starting materials. The increased purity of Si_3N_4 powder leads, in turn, to improved properties for sintered parts such as an increase in Weibull modulus and an increase in room temperature strength.

Example 22

Repeat Example 17 using two different crucible environments and a mixture of 92.31 wt% of the composite powder of Example 3, 2.35 wt% Y_2O_3, 1.16 wt% MgO, 3.50 wt% total SiO_2, 0.50 wt% ZrO_2 and 0.18 wt% Ta_2O_5. One crucible environment (Environment A) is provided by a boron nitride (BN) crucible with no surrounding powder bed. The other (Environment B) is provided by a graphite crucible painted with a BN coating and filled with a powder bed of the same composition as the mixture. Analysis of the sintered parts shows that the part sintered in Environment A has a residual carbon content of 0.10 wt% and intragranular SiC with a MND of 80 ± 40 nm and no granular SiC whereas the part sintered in Environment B has a residual carbon content of 0.39 wt%, intragranular SiC with a MND of 80 ± 40 nm and granular SiC with a MND of 220 ± 40 nm.

It is believed, without intending to be bound thereby, that the lower carbon content, and corresponding lower SiC content, resulting from sintering in Environment A is due to a reaction of granular SiC with sintering additives such as ZrO_2. This reaction appears to be suppressed by sintering in Environment B. Selection and control of the sintering environment, therefore, influence the microstructure of resulting sintered parts. Similar results are expected with other composite powders and sintering additives. Some variation is expected with changes in sintering environment and sintering additive selection and amounts. It is possible, for example, to obtain an amount of granular SiC that is intermediate between those resulting from sintering in Environments A and B by using a partial powder bed or a powder bed with a different composition than the material being sintered.

Example 23

Repeat Example 1, but use air rather than an air/nitrogen mixture to remove excess carbon. The resultant powder has a carbon content of 0.44 wt% (1.47 wt% as SiC), an oxygen content of 2.36 wt% (4.43 wt% as SiO_2) and a BET surface area of 6.8 m^2/g. The results, while not the same as those in Example 1, are believed to be within experimental error.

Place 10.8 g of the Si_3N_4 powder into a graphite crucible equipped with a 1/2 inch (1.3 cm) diameter graphite feed tube for feeding nitrogen gas through a porous distributor plate in the crucible's base. The crucible has a diameter of 2.25 in (5.7 cm) and a depth of 3 in (7.6 cm). Place the crucible and its contents in an inert atmosphere SiC tube furnace having a heated zone with a diameter of 3 in (7.6 cm) and a length of 30 in (76 cm). Heat the crucible

and its contents to a reaction temperature of 1500°C and maintain that temperature for 12 hours before analyzing the crucible contents (powder). Analysis of the powder shows a carbon content of 0.26 wt% (0.87 wt% as SiC) and an oxygen content of 1.08 wt% (2.03 wt% as SiO_2). The powder has a Si_3N_4 content of 97.1 wt%. X-ray diffraction (XRD) analysis shows that the Si_3N_4 is greater than 95 wt% alpha phase. The powder has a BET surface area of 5.2 m^2/g. SEM and TEM analysis suggest that the reduction in surface area from 6.8 m^2/g to 5.2 m^2/g is a result of reduced internal powder particle porosity. Another way of expressing reduced internal porosity is to say that the particles take on a more solid crystallite form.

Examples 24-31

Repeat Example 23, but vary the heat treatment temperature, the time at temperature or both as shown in Table VI. Table VI also shows the powder carbon, oxygen, SiC, SiO_2 and Si_3N_4 contents and powder surface area together with comparable information from Example 23.

Table VI

Example #	Temp (°C)	Time (hrs)	Oxygen (wt%)	SiO2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	Surf Area (m^2/g)
23	1500	12	1.08	2.03	0.26	0.87	97.1	5.2
24	1500	8	1.41	2.6	0.33	1.1	96.3	5.5
25	1500	4	1.47	2.8	0.36	1.2	96.0	--
26	1450	12	1.34	2.5	0.31	1.0	96.4	5.8
27	1450	8	1.40	2.6	0.32	1.1	96.3	6.0
28	1450	4	1.58	3.0	0.36	1.2	95.8	6.1
29	1400	12	1.54	2.9	0.32	1.1	96.0	6.4
30	1400	8	1.59	3.0	0.37	1.2	95.8	6.8
31	1400	4	1.79	3.4	0.41	1.4	95.2	6.9

-- means not measured

The data presented in Table VI demonstrate that higher heat treatment times and temperatures lead to lower residual SiO_2 and SiC contents than lesser times and temperatures. The data also demonstrate the feasibility of preparing Si_3N_4 powders with residual SiC contents of < 1 wt% and residual SiO_2 contents of 2 wt% or less. The data further demonstrate that an increase in heating time, heating temperature, or both leads to a decrease in powder surface area and internal porosity of the powder. Substitution of a BN crucible for the graphite crucible produces similar results.

Examples 32-37

Use three different grades (coarse, medium and fine) of high purity crystalline quartz as SiO_2 sources and acetylene carbon black as a carbon source to prepare three different precursor powder batches. The SiO_2 sources are shown in Table VII, wherein the fine grade is designated "A", the medium grade is designated "B", and coarse grade is designated "C". Grades A and B are prepared by jet milling Grade C as described hereinabove.

Table VII

Property	A (Fine)	B (Medium)	C (Coarse)
Wt% SiO_2	> 99.8	>99.8	>99.8
Surf Area (m^2/g)	5.5	0.4	0.04
Al (ppm)	<50	<50	<50
Ca (ppm)	<10	<10	<10
Fe (ppm)	<15	<15	<15
K (ppm)	<5	<5	<5
d_{10} (µm)	0.66	2.36	115.3
d_{50} (µm)	2.40	10.17	197.9
d_{90} (µm)	7.08	24.93	318.7

Prepare each precursor powder batch by placing 116.6 g of acetylene carbon black, 145.9 g of quartz (Table VII), and 15.9 g of melamine into a 6250 milliliter (ml) urethane lined milling jar half filled with Si_3N_4 milling media (5 mm average diameter). Place the jar on a roller mill and dry mill for 2 hours before separating the precursor batch from the milling media. Add 700 ml deionized water to a large flask containing a stir bar, and heat the water, with stirring, to a temperature of 80°C. Add 130 drops of an alkylphenoxy polyethoxy ethanol (commercially available as TRITON™ X-100 from Rohm and Haas Company) and 60 drops of a silicon foam suppressing compound (commercially available as ANTIFOAM™ B from Dow Corning Corporation) while continuing stirring. Add the precursor powder batch and continue stirring for 15 minutes. Return the milling media to the jar and, after cooling the contents of the flask to ambient temperature, add them to the jar and wet ball mill the contents for 3 hours. After milling is complete, remove the contents, place them in a quartz tray and place the tray into a convection oven to dry overnight (14 hours) at 135°C.

After cooling back to ambient temperature, place the contents of the tray into the ball mill (now dry) and add 21.6 g of wheat starch and 9.8 g of corn starch. Dry mill the contents for 1 hour before recovering the resultant mixture from the milling media. Place the

resultant mixture into a mortar, add 120 g of deionized water and blend the mortar contents with a pestle to prepare an extrudable mixture. Convert the mixture to wet pellets having a diameter of 0.25 inch (0.6 cm) and a length of 0.5 inch (1.3 cm) using an extruder and cutting the extrudate with a razor blade. Convert the wet pellets into calcined pellets as in Example 1.

Use the apparatus and procedure of Example 23, but reduce the time at reaction temperature from 12 hours to 5 hours and use a temperature of either 1470°C or 1500°C to convert 15.0 g of calcined pellets prepared from each precursor powder batch into a product. Remove excess carbon as in Example 1, but increase the temperature from 700°C to 800°C and reduce the time at temperature from 3 hours to 2 hours.

Analysis of each product provides results shown in Table VIII. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase. The product of Example 32 has a SiC content of 1.7 wt%, a SiO_2 content of 18.2 wt% and a Si_3N_4 content of 80.1 wt%.

Table VIII

Example #	SiO_2 Type	Rxn Temp (°C)	Oxygen (wt%)	SiO_2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	S.A. (m^2/g)
32	A	1470	9.7	18.2	0.51	1.7	80.1	--
33	A	1500	3.2	6.0	0.61	2.0	92.0	10.9
34	B	1470	11.9	22.3	0.42	1.4	76.3	--
35	B	1500	2.7	5.1	0.58	1.9	93.0	12.3
36	C	1470	14.8	27.8	0.42	1.4	70.8	--
37	C	1500	6.1	11.4	0.53	1.8	86.8	10.7

-- means not measured

The data in Table VIII demonstrate that the high purity quartz used as a starting material should be of a fine grade, preferably with a S.A. > 0.2 m^2/g and a mean particle size (d_{50}) < 15 μm in order to obtain high levels of conversion (< 3 wt% residual monatomic O) and low levels of nanophase SiC (< 2 wt% SiC, < 0.6 wt% C as SiC). If greater SiC contents are desired, higher temperatures should be used. If higher residual oxygen contents are desired, coarser grades of high purity quartz should be used.

Examples 38-41

Repeat the procedure of Examples 32-37, but add 29.2 g of a composite powder prepared as in Example 3 as a seed prior to the initial dry ball milling step. Table IX collects data for these examples. SEM/TEM analysis of the resultant powders shows the presence of fine (0.2 μm MND) α-Si_3N_4 crystallites without any protruding β-Si_3N_4 fibers and of less than 50 nm (MND) SiC crystallites. XRD shows that the Si_3N_4 is greater than 95% α-Si_3N_4. X-Ray fluorescence (XRF) analysis of the resultant powders shows that they contain less than 100 ppm

Ca, less than 50 ppm Al, less than 50 ppm Fe, less than 20 ppm S, less than 10 ppm Cl, less than 10 ppm F and less than 10 ppm K.

Table IX

Example #	SiO_2 Type	Rxn Temp (°C)	Oxygen (wt%)	SiO_2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	S.A. (m^2/g)
38	A	1470	1.6	3.0	0.52	1.7	95.3	8.0
39	A	1500	1.8	3.4	0.59	2.0	94.6	7.4
40	B	1470	2.2	4.1	0.48	1.6	94.3	8.2
41	B	1500	1.7	3.2	0.55	1.8	95.0	7.9

The data in Table IX demonstrate that a fine, high purity, substantially α-Si_3N_4 powder having no β-Si_3N_4 fibers protruding from α-Si_3N_4 crystallites, less than 2 wt% monatomic oxygen and less than 2 wt% nanophase SiC (less than 50 nm MND) can be synthesized from admixtures of high purity, fine carbon (such as acetylene carbon black), high purity, fine crystalline quartz and Si_3N_4 seed crystallites.

Examples 42-44

Use three different carbon sources and a high purity crystalline quartz having a SiO_2 content in excess of 99.8 wt%, a surface area of 1.9 m^2/g, and impurity levels (Al, Ca, Fe and K) equal to or lower than those shown in Table VII to prepare precursor powder batches. The carbon sources are listed in Table X, wherein a large particle size material (commercially available from R. T. Vanderbilt as THERMAX™ Ultra Pure) is designated "A", acetylene carbon black (the same as in Example 1) is designated "B", and an intermediate particle size material (commercially available from Cabot Corporation as MONARCH™ 120) is designated "C". A mathematical symbol (<) is used as an abbreviation for less than in Table X and elsewhere. Other mathematical symbols such as (>) are also used herein.

Table X

Property	Carbon A	Carbon B	Carbon C
Wt% C	98.9	98.6	96.0
Wt% O	0.3	0.3	0.6
DBP Absorption ($cm^3/100g$)	33	250	25
Al (ppm)	<10	<10	32
Ca (ppm)	<10	<10	155
Cl (ppm)	<10	<10	65
Fe (ppm)	7	12	40
Na (ppm)	<200	<200	340
S (ppm)	<10	<10	1.67 wt%
Si (ppm)	18	<10	16
Average Particle Size (μm)	0.22	0.03	0.06
Surface Area (m^2/g)	8	72	25

Prepare each precursor powder batch with a different carbon source using the component amounts and procedure outlined in Example 32. Convert the powder batches to product powder using the procedure of Example 32, but reduce the temperature to 1435°C. Analysis of each product provides results shown in Table XI. XRD analysis shows the Si_3N_4 to be greater than 95% alpha phase.

Table XI

Sample #	Carbon Type	Oxygen (wt%)	SiO_2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	SiC MND (nm)	SiC Size Range (nm)
42	A	4.2	7.9	1.8	6.0	86.1	90	70 - 150
43	B	3.1	5.8	1.1	3.7	90.5	50	30 - 100
44	C	2.1	3.9	4.4	14.7	81.4	80	30 - 100

The data in Table XI demonstrate that SiC size depends, to some extent, upon starting carbon particle size. The amount of SiC may be influenced by other factors, such as the level of impurities in carbon type C (Table X) or temperature (Table II).

Example 45 (Rod-like β-Si_3N_4 Crystallites)

Prepare wet pellets as in Example 1 using 116.6 grams (g) of acetylene carbon black, 145.9 g of quartz (Grade B, Table VII), 29.2 g of Si_3N_4 having a β-phase content of 81.2 wt% (commercially available from Shin Etsu Chemical Company as KSN80SP), 17.2 g of melamine, 24.0 g wheat starch, 10.3 g of corn starch and 200 g of deionized water. Place the wet pellets into a forced air convection oven and dry them overnight (14 hours) at 135°C. Place the dried pellets into a tube furnace with flowing nitrogen gas and heat for 5 hours at 330°C to calcine the starches and melamine.

Convert 9.2 g of the calcined pellets into a powder using the procedure of Example 32 with a reaction temperature of 1500°C and a time at that temperature of 5 hours. Analysis after removal of excess carbon shows a carbon content of 0.45 wt% (1.5 wt% as SiC), an oxygen content of 1.5 wt% (2.8 wt% as SiO_2) and a BET surface area of 12.1 m^2/g. A mass balance indicates that the product has about 3.0 g of Si_3N_4 over the amount of seed Si_3N_4. Calculations based upon XRD peak area analysis shows that the product has an α-Si_3N_4 content of 64.8 wt% and a corresponding β-Si_3N_4 content of 35.2 wt%.

Example 46 (Rapid Heating)

Place 10.3 g of the calcined pellets prepared in Example 45 into a feed tube maintained at room temperature (taken as 25°C) and located above a high temperature graphite crucible that is maintained at a temperature of 1435°C. Gaseous nitrogen flows through a perforated distributor in the crucible's base at a rate of 6 slpm. Open a ball valve in the feed tube to add the room temperature pellets to the heated crucible from above. Maintain the crucible and its contents at the 1435°C for 5 hours. Remove the pellets from the

crucible and remove excess carbon as in Examples 32-37. The resulting powder has a carbon content of 0.88 wt% (2.9 wt% as SiC) and an oxygen content of 2.67 wt% (5.0 wt% as SiO_2), based on powder weight. XRD analysis shows the presence of both α-Si_3N_4 and β-Si_3N_4 in amounts similar to those in Example 45.

Analysis of the powders of Examples 45 and 46 by SEM and TEM shows the presence of both α-Si_3N_4 and β-Si_3N_4. Characterization of the powder of Example 45 reveals the presence of α-Si_3N_4 and β-Si_3N_4 crystallites, the β-Si_3N_4 crystallites having a MND of about 0.045 μm and a mean aspect ratio of 5.4/1, the aspect ratio ranging between 1.5/1 and 9/1 (a length within a range of from 0.08 to 0.5 μm, with a mean of 0.24 μm). The α-Si_3N_4 crystallites have a MND 0.17 μm, the MND ranging from 0.03 to 0.46 μm. Characterization of the powder of Example 46 reveals the presence of α-Si_3N_4 and β-Si_3N_4 crystallites, the β-Si_3N_4 crystallites having a MND of about 0.036 μm and a mean aspect ratio of 7.6/1, the aspect ratio ranging between 3/1 and 21/1 (a length within a range of from 0.05 to 1.1 μm, with a mean of 0.27 μm). The α-Si_3N_4 crystallites have a MND 0.12 μm, the MND ranging from 0.05 to 0.22 μm.

If a composite powder prepared as in Example 13 ($y = 0.26$) and a composite powder prepared as in Example 45 with a y value of 0.26 are both sintered as in Example 16, the composite powder prepared as in Example 45 reaches a density of 97 percent of theoretical density in 3 hours whereas the composite powder prepared as in Example 13 requires nearly 9 hours to attain the same density. The composite powder containing both α-Si_3N_4 and β-Si_3N_4 crystallites (the β-Si_3N_4 crystallites being rod-like) is therefore more sinterable than a composite powder lacking the rod-like β-Si_3N_4 crystallites.

If the seed is changed to that used in Example 1, the product has an α-phase Si_3N_4 content in excess of 95 wt%. The β-phase Si_3N_4 in such a product contains no rod-like crystallites. Changing the seed to a blend of 75 wt% of the seed used in Example 1 and 25 wt% of the seed used in Examples 45 and 46, yields a product having an α-phase Si_3N_4 content of 90.5 wt% and a β-phase Si_3N_4 that contains no rod-like crystallites. In addition, heating the seed used in Example 46 at 1500°C for 5 hours fails to produce any rod-like crystallites.

The foregoing results demonstrate that using a high β-phase Si_3N_4 seed yields a product that differs from those obtained with a high α-phase Si_3N_4 seed or a seed that is a blend of the high β-phase Si_3N_4 seed and the α-phase Si_3N_4 seed. The blend effectively dilutes the β-phase Si_3N_4 content to a level of less than 75 wt%, based upon seed weight. The rod-like β-Si_3N_4 crystallites appear only when the seed has a β-phase Si_3N_4 content in excess of 75 wt%, based upon seed weight. Nucleation of fine solid α-Si_3N_4 crystallites and formation of rod-like β-Si_3N_4 crystallites occur either with slow heating as in Example 45 or rapid heating as in Example 46.

Example 47 (Rapid Heating)

Prepare calcined pellets as in Example 45, but use a quartz having > 99.8 wt% SiO_2 with a mean particle size (d_{50}) of < 10 μm and change the seed to a crystalline α-phase Si_3N_4 powder (UBE Industries Ltd., as SN E-3). The quartz particle size is obtained in the same manner as silicas A and B in Table VII. The calcined pellets contain carbon at a level of 100% excess over that required to carbothermally reduce the SiO_2. The pellets contain sufficient Si_3N_4 to provide a seed/SiO_2 ratio of 0.2/1.

Convert 10.7 g of the calcined pellets using the apparatus and procedure of example 46, but reduce the excess carbon removal temperature to 700°C. It is estimated that external pellet surfaces are heated at a rate in excess of 100°C/second. Maintain the crucible and its contents at 1435°C for 5 hours. The resulting powder has a carbon content of 0.65 wt% (2.17 wt% as SiC) and a monatomic oxygen content of 2.56 wt% (4.81 wt% as SiO_2), based on powder weight. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase. Analysis by Field Emission Gun Scanning Electron Microscopy (FEG/SEM) shows the powder to be composed of Si_3N_4 crystallites having a MND of 0.32 ± 0.1 μm. There appears to be a substantial number of fine α-phase Si_3N_4 crystallites that have a MND less than the seed particles present in the powder.

Duplicate this Example, but use the slower heating procedure of Example 1, to produce Si_3N_4 crystallites that are larger than those of this Example 47 and contain few, if any, new, fine crystallites.

Example 48-50 (No Seed)

Using the component amounts, omitting the Si_3N_4 seed, and procedures of Examples 32-37, prepare precursor powder batches from three different SiO_2 sources and acetylene carbon black. Table XII shows the SiO_2 sources. High purity crystalline quartz (obtained in the same manner as A and B in Table VII) is designated "A"; low purity crystalline quartz is designated "B"; and high purity amorphous quartz is designated "C".

Table XII

Property	Silica A	Silica B	Silica C
Wt% SiO_2	>99.8	99.3	> 99.8
Surf Area (m^2/g)	1.9	2.2	204
Al (ppm)	18	640	<2
Ca (ppm)	<2	290	<2
Fe (ppm)	<2	360	<2
K (ppm)	<1	360	<1
P (ppm)	<2	23	<3
Ti (ppm)	<2	79	<2

Convert 10.4 g of each precursor powder batch into a product using the procedure and conditions of Example 42-44. Analysis of each product provides results shown in Table XIII. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase.

Table XIII

Sample #	SiO_2 Type	Oxygen (wt%)	SiO_2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	Protruding β-Si_3N_4 Fibers Present
48	A	3.1	5.8	1.1	3.7	90.5	Trace
49	B	3.5	6.6	0.6	2.0	91.4	Yes
50	C	3.5	6.6	1.4	4.7	89.3	Yes

The data in Table XIII demonstrate that the presence of β-Si_3N_4 fibers or whiskers protruding from α-Si_3N_4 crystallites depends upon crystallinity, purity and particle size of starting SiO_2 used to prepare the Si_3N_4 product. Only trace amounts of β-Si_3N_4 fibers result when using high purity, medium particle size crystalline SiO_2 whereas much larger, readily discernible amounts result when using either crystalline SiO_2 of lower purity or amorphous SiO_2 as a starting material. Similar results are expected with other compositions that are disclosed herein, including those with a seed material such as Si_3N_4.

Example 51

Repeat Example 45, but change the seed to that used in Example 47, to prepare a product powder having a carbon content of 0.72 wt% (2.4 wt% as SiC) and an oxygen content of 1.38 wt% (2.6 wt% as SiO_2). XRD analysis shows the Si_3N_4 to be greater than 95% alpha phase. TEM/SEM analysis of the product indicates an α-Si_3N_4 crystallite MND of 0.68 µm. TEM analysis shows a SiC crystallite MND of less than 50 nm.

Example 52

Repeat Example 51, but change the seed to that used in Example 1, to prepare a product powder having a carbon content of 0.47 wt% (1.6 wt% as SiC) and an oxygen content of 1.28 wt% (2.4 wt% as SiO_2). XRD analysis shows the Si_3N_4 to be greater than 95% alpha phase. TEM/SEM analysis of the product indicates an α-Si_3N_4 crystallite MND of 0.25 µm.

Examples 51 and 52 demonstrate that α-Si_3N_4 seed MND strongly influences product α-Si_3N_4 crystallite MND. The smaller starting material MND in Example 52 leads to a product MND that is smaller than that of Example 51. The examples suggest that a seed α-Si_3N_4 crystallite MND of less than 0.15 µm favors synthesis of high purity (low metals and < 2 wt% monatomic oxygen) α-Si_3N_4 powder with a crystallite MND of < 0.3 µm.

Examples 53-58

Repeat Example 52, but vary the amount of α-Si_3N_4 seed from no seed in Example 53 to an amount sufficient to provide a seed/SiO_2 ratio in the starting material of 0.6:1 in Example 58. Table XIV shows the seed/SiO_2 ratio and the product α-Si_3N_4 crystallite MND. Table XIV includes comparable data from Example 52.

Table XIV

Example Number	Seed/SiO_2 Ratio	Product α-Si_3N_4 MND (µm)
53	0.0	0.72 ± 0.21
54	0.05	0.45 ± 0.13
55	0.1	0.41 ± 0.09
52	0.2	0.25 ± 0.07
56	0.3	0.18 ± 0.06
57	0.4	0.20 ± 0.07
58	0.6	0.19 ± 0.07

The data in Table XIV suggest that product α-Si_3N_4 crystallite MND can be controlled by the addition of seed α-Si_3N_4. High seed/SiO_2 ratios spread growth out over more crystallites than are available with low seed/SiO_2 ratios and lead to smaller product crystallite

MND's than those resulting from low seed/SiO_2 ratios or no seed. The data also suggest that a seed/SiO_2 ratio of greater than about 0.15 promotes products having an α-Si_3N_4 crystallite MND of < about 0.3 μm, especially when combined with a seed α-Si_3N_4 crystallite MND of < about 0.2 μm. Although the latter products may be preferred for many applications, the products that result when no seed is used or the seed/SiO_2 ratio is very low (< 0.15) are also suitable for use in some applications.

Examples 59-64

Prepare six batches of calcined pellets using the procedure and component amounts of Examples 32-37 and two different high purity carbon sources (Carbon A and Carbon C from Table X) and two different high purity SiO_2 sources (Silica A and Silica C from Table XII), both with and without the same Si_3N_4 seed as in Example 1. Use the same apparatus and procedure as in Examples 32-37, but reduce the temperature to 1435°C, to convert 10.4 g of each batch of calcined pellets into a product powder. Table XV identifies the carbon and SiO_2 sources, states whether or not the precursor powder batch contains a seed, and specifies the crystallite MND for both Si_3N_4 and SiC.

Table XV

Example #	Carbon Type	Silica Type	Seed Present	Si_3N_4 MND (μm)	SiC MND (nm)
59	A	A	No	0.5	90
60	A	A	Yes	0.2	80
61	B	A	No	0.7	50
62	B	A	Yes	0.2	40
63	B	C	No	1.2	35
64	B	C	Yes	0.4	50

Analysis of Example 61 shows a carbon content of 1.1 wt% (3.7 wt% as SiC) and an oxygen content of 3.1 wt% (5.8 wt% as SiO_2). XRD analysis shows the Si_3N_4 to be greater than 95% alpha phase. SEM/TEM analysis of the product shows that the Si_3N_4 crystallites fall within a size range of 0.4 to 1.1 μm with a crystallite MND of about 0.7 ± 0.2 μm. The SiC crystallites are within a range of 30 to 100 nm with a MND of about 50 nm.

Analysis of Example 62, which differs from Example 61 by containing seed Si_3N_4, reveals a carbon content of 0.5 wt% (1.7 wt% as SiC), an oxygen content of 2.0 wt% (3.8 wt% as SiO_2). The Si_3N_4 crystallite size falls within a range of 0.1 to 0.5 μm with a crystallite MND of about 0.2 ± 0.1 μm. The SiC crystallites are within a range of 20 to 90 nm with a crystallite MND of about 40 nm.

The data in Table XV demonstrate that use of a moderate surface area crystalline quartz as the SiO_2 source, acetylene black as the carbon source and a seed in the precursor assures synthesis of a fine composite powder wherein the Si_3N_4 crystallite MND is about 0.2 μm and the SiC crystallite MND is about 50 nm. In the absence of a seed, as in Example 61, product crystallite size tends to be larger than when seed is present (Example 62). Similarly, a larger starting carbon leads to comparatively larger SiC crystallites. Although a fine product crystallite size is desirable for many applications, products with comparatively large crystallite size are also useful for some applications.

If high purity amorphous SiO_2 (Silica C) is substituted for high purity crystalline SiO_2 (Silica A), it should promote Si_3N_4 growth. It should also result in larger Si_3N_4 crystallites in the product.

Examples 65-67

Prepare six batches of calcined pellets using the procedure and component amounts of Examples 59-64, the carbon sources of Table X, and Silica A from Table XII. Use the apparatus and procedure of Examples 59-64 to convert 10.5 g of each batch of calcined pellets into a product powder. Table XVI identifies the carbon (C) source, and provides product powder carbon and oxygen contents, with equivalent SiC and SiO_2 contents. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase. SEM/TEM analysis of the Si_3N_4 crystallites reveals micropores of a size approximating that of the carbon source.

Table XVI

Example #	C Source	Average C Particle Size (μm)	Carbon (wt%)	Oxygen (wt%)	SiC (wt%)	SiO_2 (wt%)	Si_3N_4 Micropore Size (μm)
65	A	0.22	4.4	2.1	14.7	3.9	0.25
66	B	0.03	1.1	3.1	3.7	5.8	0.03
67	C	0.06	1.8	4.2	6.0	7.9	0.06

The results in Table XVI demonstrate that micropore size depends upon size of the carbon source. In other words, the largest micropores result from using the largest carbon source (Source A), while the finest micropores result from using the smallest carbon source (Source B). If precursors contain similar mass amounts of carbon, fine carbon crystallites should lead to Si_3N_4 crystallites with more pores than result from use of larger (coarser) carbon crystallites.

Example 68

Repeat Example 47 using 10.6 g of calcined pellets prepared from a combination of 302 grams (g) of acetylene carbon black, 378 g of high purity quartz, 40 g of melamine, 56 g of wheat starch, 24 g of corn starch and 520 g of deionized water. All starting materials are the same as those used in Example 1. The resulting powder has a carbon content of 0.8 wt% (2.7 wt% as SiC) and an oxygen content of 2.4 wt% (4.5 wt% as SiO_2), based on powder weight. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase. A TEM photomicrograph shows the powder contains nanophase SiC having a MND of about 50 nm. The powder has a BET surface area of 11.8 m^2/g.

Example 69

Repeat Example 6, but preheat the crucible to a temperature of 1500°C and maintain that temperature for a period of 10 minutes before reducing the temperature to that of Example 68 for a period of 7 hours. The resultant powder has a carbon content of 4.7 wt% (15.7 wt% as SiC) and an oxygen content of 2.0 wt% (3.8 wt% as SiO_2), based on powder weight. XRD analysis shows the presence of SiC. TEM shows the presence of fine SiC crystallites dispersed in the Si_3N_4. The powder has a BET surface area of 12.9 m^2/g.

Example 70-73

Repeat Example 69, but vary the initial preheat temperature and time at that temperature as shown in Table XVII. Table XVII also shows carbon and oxygen contents of the powder, equivalent weight percentages of SiC and SiO_2, Si_3N_4 content and powder S.A. and includes comparable data for Examples 68 and 69.

Table XVII

Example #	Pre-heat Time (min)	Pre-heat Temp (°C)	Oxy-gen (wt%)	SiO_2 (wt%)	Car-bon (wt%)	SiC (wt%)	Si_3N_4 (wt%)	Pow-der S.A. (m^2/g)
68	0	1435	2.4	4.5	0.8	2.7	92.8	11.8
69	10	1500	2.0	3.8	4.7	15.7	80.5	12.9
70	5	1525	3.1	5.8	6.8	22.7	71.5	12.9
71	15	1525	4.5	8.4	7.1	23.7	67.9	12.2
72	5	1475	2.6	4.9	1.6	5.3	89.8	12.3
73	15	1475	2.1	3.9	3.2	10.7	85.4	12.2

A comparison of Example 68 with Examples 69-73 shows the elevated initial temperatures of Examples 69-71 promote the formation of SiC. Examples 72 and 73 show that preheating temperatures below 1500°C, e.g. 1475°C, also yield levels of SiC that exceed those attained in the absence of preheating. Lower preheating temperatures should provide similar results if preheating times are increased to compensate for slower rates of SiC production. The SiC formed at the initial high temperature should serve as a seed or catalyst for the subsequent carbothermal synthesis of α-Si_3N_4.

Examples 74-83 (Varying Amounts of Seed and Excess Carbon Content)

Use the procedure of Example 47 to prepare five different precursor powder batches with varying amounts, all of which are shown in Table XVIII, of acetylene carbon black, high purity quartz (>99.8 wt% SiO_2 with a mean particle size (d_{50}) of 5.1 µm), and a crystalline α-phase Si_3N_4 powder (prepared as in Example 2 with a mean particle size (d_{50}) of 0.86 µm and a BET surface area of 7.46 m^2/g), together with 28.0 g wheat starch, 12.0 g corn starch and 20.0 g melamine. Convert each powder batch to calcined pellets as in Example 47, but increase the deionized water to 300 g. Table XVIII also shows % excess carbon and ratio of seed/SiO_2 ratio in each batch of calcined pellets.

Table XVIII

Component or Property	Precursor Number				
	1	2	3	4	5
Carbon (g)	113.2	113.2	113.2	154.4	78.4
Silica (g)	141.6	113.3	188.8	154.5	130.7
Si_3N_4 seed (g)	85.0	113.3	37.8	30.9	130.7
% Excess Carbon	100	150	50	150	50
Seed/SiO_2 Ratio	0.6:1	1.0:1	0.2:1	0.2:1	1.0:1

Use the procedure of Example 47 and a temperature/time combination of either 1435°C for 5 hours or 1400°C for 7 hours to convert a 10.3 g portion of each batch of calcined pellets to a product. Table XIX presents data relating to each example. The powder of Example 74 has an equivalent SiC content of 2.84 wt% and an equivalent SiO_2 content of 2.78 wt%. Equivalents for the other examples are readily determined without undue experimentation. XRD analysis shows the Si_3N_4 to be greater than 95% -phase.

Table XIX

Example #	Precursor #	Excess C (%)	Seed/SiO_2 Ratio	Temp (°C)	Residual C (wt%)	Residual O (wt%)	Powder Surf Area (m^2/g)
74	1	100	0.6:1	1435	0.85	1.48	6.70
75	2	150	1.0:1	1435	0.63	1.28	6.20
76	3	50	0.2:1	1435	1.1	1.67	8.44
77	4	150	0.2:1	1435	0.61	2.89	9.85
78	5	50	1.0:1	1435	0.71	1.39	5.18
79	1	100	0.6:1	1400	0.57	1.58	6.54
80	2	150	1.0:1	1400	0.54	1.12	5.90
81	3	50	0.2:1	1400	0.88	1.61	8.40
82	4	150	0.2:1	1400	0.57	2.61	9.60
83	5	50	1.0:1	1400	0.65	1.23	5.19

The data in Table XIX demonstrate that, for a given Si_3N_4 seed, an increase in % excess carbon and a decrease in seed/SiO_2 ratio both yield a higher surface area Si_3N_4 product powder. Conversely, a decrease in % excess carbon and an increase in seed/SiO_2 ratio both yield a lower surface area Si_3N_4 product powder. As such, a desired product surface area can be attained via adjustment of the % excess carbon and seed/SiO_2 ratio. Similar results are expected with other Si_3N_4 seed materials and precursor compositions.

Example 84-92

Use the procedure of Example 47 to prepare a primary batch powder from 302 g of acetylene carbon black, 378 g of the same quartz as in Example 1 and 40 g of melamine. Also as in Example 47, convert 220 g of the primary batch powder, 17.1 g wheat starch, 7.3 g corn starch and 173 g of deionized water into calcined pellets of a first precursor (P-1). Prepare a second precursor (P-2) by placing 250 g of the primary batch powder in the same milling jar used to prepare the primary batch powder together with the same size milling media and 15.8 g of Si metal (Elkem HQ SILGRAIN™, <10 µm average particle size) and dry ball milling for two hours before separating the resulting powder mixture from the milling media. Convert this powder mixture, 20.7 g wheat starch, 8.9 grams corn starch and 181 g deionized water into calcined pellets using the same procedure as in preparing P-1. The calcined pellets have a Si/SiO_2 ratio of 0.12. Prepare a third precursor (P-3) in the same manner as used for P-2, but increase the amount of Si metal to provide calcined pellets having a Si/SiO_2 ratio of 0.36.

Convert 10.2 g of P-1 pellets into a powder (Example 84) using the procedure of Example 47. The powder has a carbon content of 1.2 wt% (4.0 wt% as SiC) and an oxygen content of 2.3 wt% (4.3 wt% as SiO_2), based on powder weight. XRD analysis shows the Si_3N_4 to be greater than 95% α-phase. A SEM photomicrograph shows the powder contains crystallites having a diameter of about 1 μm.

Repeat Example 84, but vary the time at temperature or the precursor or both, as shown in Table XX, to prepare Examples 85-92. Table XX shows selected data for Examples 84-92.

Table XX

Example #	Precursor	Time (hrs)	Oxygen (wt%)	SiO_2 (wt%)	Carbon (wt%)	SiC (wt%)	Si_3N_4 (wt%)
84	P-1	5	2.3	4.3	1.2	4.0	91.7
85	P-1	6	2.1	3.9	0.9	3.0	93.1
86	P-1	7	2.1	3.9	0.9	3.0	93.1
87	P-2	5	2.9	5.4	7.3	24.4	70.2
88	P-2	6	2.6	4.9	7.6	25.4	69.7
89	P-2	7	2.7	5.1	9.0	30.0	64.9
90	P-3	5	3.3	6.2	18.2	60.7	33.1
91	P-3	6	3.4	6.4	17.6	58.7	34.9
92	P-3	7	3.3	6.2	18.1	60.4	33.4

The data presented in Table XX demonstrate that the presence of Si metal influences the amount of SiC produced via carbothermal synthesis. The data also show that powders having a residual monatomic oxygen content of < 4.0 wt% and a SiC content > 0.5 wt% are readily produced in accordance with the present invention.

Example 93

Prepare a pressureless sinterable composition using the powder of Example 3 and the following formulation, wherein all weight percentages are based upon composition weight and all components are in powder form: 95.6 wt% Si_3N_4; 2.31 wt% Y_2O_3; 1.17 wt% MgO; 0.24 wt% SiO_2; 0.5 wt% ZrO_2; and 0.18 wt% Ta_2O_5. The amount of SiO_2 reflects the added amount rather than the amount of SiO_2 contributed by the Si_3N_4 powder of Example 3. If that amount is included, the composition has a total SiO_2 content of 3.5 wt%. Attrit the composition components for one hour in ethanol using zirconia milling media to prepare an attrited mixture. Dry the attrited mixture using a rotary evaporator and separate the attrited mixture from the milling media using a 35 mesh (425 μm sieve opening) stainless steel sieve.

Convert the mixture into test pieces by uniaxial pressing at about 2500 pounds per square inch (psi) (about 17 megapascals (MPa)) followed by isostatic pressing at about 40,000 psi (about 276 MPa).

Place the test pieces into a BN painted graphite crucible and surround them with a powder bed of the same composition as the test pieces. Sinter the pieces for 12 hours in a 4 inch (10 cm) ASTRO graphite furnace at 1750°C under a one atmosphere (about 100 kilopascals (KPa)) flowing nitrogen atmosphere.

TEM analysis of the sintered pieces shows a SRS structure that contains residual SiC particles. The SiC particles are distributed throughout a SRS matrix and located in a glassy grain boundary phase at triple point junctions of Si_3N_4 grains (granular) and within Si_3N_4 grains (intragranular). Based upon the Si_3N_4 powder's carbon content, the sintered pieces contain about 1.4 wt% SiC reinforcement, based upon sintered piece weight.

Cut a section from a sintered piece and polish a surface to a mirror finish using, in succession, diamond pastes having an average particle size of 15 μm, 6 μm and 1 μm. Indent the polished surface with a 30.4 pound (lb) (about 14 kg) load using a diamond Vicker's indentor. From the indent, the Palmqvist toughness of the material is determined to be 44.2 kg/mm. If Si_3N_4 powder, such as that used as a seed in Example 1, is used in place of the composite powder of the present invention, the resultant sintered body has a lower Palmqvist toughness even with the same total SiO_2 content, additions of SiC powder or both. Similar results are expected with other powders produced as described herein as well as with other physical properties.

Example 94

Prepare a series of SRS materials via hot pressing using a modification of the procedure described in Example 1 of U.S. 4,883,776 (column 12, line 31 through column 14, line 17). The relevant teachings of U.S. 4,883,776 are incorporated herein by reference. The modifications include: an applied pressure of 500 pounds per square inch gauge (psig) (3.4 MPa) rather than 1000 psig (6.9 MPa) while heating from ambient temperature to 1200°C over a period of 60 minutes rather than 30 minutes; an increase to a temperature of 1850°C over a period of 50 minutes rather than to 1825°C over a period of 40 minutes; and a time at maximum temperature of one hour rather than 45 minutes. Each material is prepared according to the following formulation wherein all percentages are based upon composition weight: 85.78 wt% of a combination of Si_3N_4 and SiC powders; 5.84 wt% Y_2O_3; 3.22 wt% MgO; 0.32 wt% CaO; and 4.84 wt% total SiO_2 (added powder plus SiO_2 introduced by the Si_3N_4 powder). Prepare four powders as in Example 1, but vary the temperature and increase the time at temperature to 390 minutes. The resulting powders, their SiC contents and their designation are, respectively: 1450°C, 1.38 wt%, and A-1; 1470°C, 3.89 wt%, and A-2; 1480°C, 5.28 wt%, and A-3; and 1490°C, 19.78 wt%, and A-4. Physically admix SiC (0.18 μm average particle size by direct measurement from SEM photos, Ferro Corp.) with the Si_3N_4 powder used

as a seed in Example 1 to provide respective SiC contents and designations of: 0.0 wt%, B-1; 3.50 wt%, B-2; and 7.00 wt%, B-3. Repeat the procedure used for B-1 through B-3, but change the Si_3N_4 powder to a direct nitrided powder (H. C. Starck Inc. as designation LC12N) to provide respective SiC contents and designations of: 0.0 wt%, C-1; 3.50 wt%, C-2; and 7.00 wt%, C-3. The SiC is the same as that used in Powder B. Powder D-1 is the same as Powder A-1 with an added 2.26 wt% of the same SiC powder as in Powder B-2. Table XXI shows the average room temperature (about 25°C) strength, elevated temperature strength (1300°C) and percent of room temperature strength retained at 1300°C for several of the materials. Table XXII contrasts SiC content of several of the materials with average strain to failure, average fracture toughness values and average room temperature fracture strength. Table XXIII summarizes TEM results for two of the materials. The nitrogen content is determined by parallel electron energy loss spectroscopy (parallel EELS) with a GATAN Model 666 spectrometer fitted to either a VG HB601UX STEM operated at 100 kilovolts (kV) or an ABT EM-002B operated at 200 kV. R. F. Egerton, in Electron Energy Loss Spectroscopy in the Electron Microscope (1986), describes an approach wherein the nitrogen and carbon EELS signals for each particle are integrated and the nitrogen/carbon atomic ratio is calculated. The GATAN software follows this approach. Thus, the nitrogen values (2-10 wt%) reported herein reflect the use of this computational approach. The wt% nitrogen in SiC is then calculated directly from the atomic ratios.

Table XXI

Si_3N_4 Powder	SiC Content (wt%)	Strength (Room Temp) (MPa)	Strength (1300°C) (MPa)	% of Room Temp Strength Retained at 1300°C
A-1	1.38	935	563	60
A-2	3.89	832	565	68
A-3	5.28	1045	505	48
B-1	0.0	1005	505	50
B-2	3.5	1128	563	50
B-3	7.0	905	523	57
C-1	0.0	835	308	37
C-2	3.5	740	283	38
C-3	7.0	795	261	33

Table XXII

Si_3N_4 Powder	SiC Content (wt%)	% Strain at Failure	Fracture Toughness ($MPa.m^{1/2}$)	Fracture Strength (MPa)
A-1	1.38	0.78	7.73	935
A-2	3.89	0.75	*	*
A-3	5.28	0.71	7.41	1045
A-4	19.78	0.69	7.77	1090
B-1	0.0	*	8.11	1050
B-2	3.5	0.92	7.35	1125
B-3	7.0	0.78	6.75	905
C-1	0.0	1.34	7.43	835
C-2	3.5	0.94	6.77	740
C-3	7.0	0.82	6.02	795
D-1	3.64	*	7.06	*

* means no sample prepared for this test

Table XXIII

	Powder A-2	Powder B-2
SiC Content (wt%)	3.89	3.5
Size of Granular/Triple Point SiC (nm)	100-500	100-400
Size of Intragranular SiC (nm)	40-240	70-280
Distribution of Triple Point SiC	Clustered	Isolated
Glass Phase O/Si ratio	0.65:1	0.90:1
Nitrogen in Intragranular SiC	Yes	No

The data in Tables XXI through XXIII illustrate several points. First, as shown in Table XXI, SRS materials prepared with composite powders of the present invention have a greater retention of high temperature strength (MPa) at SiC contents of 3.89 wt% or 1.38 wt% than those prepared with physical mixtures of 3.5 wt% or 7.0 wt% submicrometer SiC powder and either diimide derived Si_3N_4 powders or direct nitrided Si_3N_4 powders. Second, Table XXII shows that SRS materials prepared with composite powders of the invention have greater creep resistance at a given SiC content than those prepared with physical mixtures of

submicrometer SiC powder and either diimide derived Si_3N_4 powders or direct nitrided Si_3N_4 powders. Creep resistance is inversely proportional to strain at failure. A SiC addition of 7.0 wt% to a diimide derived Si_3N_4 powder is required to attain the same creep resistance as a composite powder having a SiC content of 1.38 wt%. Table XXII also shows that physical additions of SiC decrease fracture toughness and, to a lesser extent, room temperature strength of SRS materials. Table XXIII highlights microstructural differences between an SRS material prepared from a composite powder of the invention and an SRS material prepared by physically admixing SiC powder into a composition based upon a diimide derived Si_3N_4 powder. These microstructural differences are believed, at least in part, to account for the differences disclosed by reviewing Tables XXI through XXIII. An additional difference is that at least a portion of the intragranular SiC in the SRS material prepared with powder A-2 (Table XXIII) contains about 3.3 wt% residual nitrogen (as measured by parallel EELS) whereas the intragranular SiC in the SRS material prepared with powder B-2 (physically mixed SiC) does not. This residual nitrogen presumably comes from the SiC portion of the composite powders prepared as described herein. As such, it is expected in all SRS bodies prepared from composite powders of the present invention. Similar results are expected with other composite powders prepared as described herein.

Example 95

Repeat Example 5, but change the reaction temperature from 1475°C to 1500°C. The resulting powder has a carbon content of 1.59 wt% (5.3 wt% as SiC), based upon powder weight. TEM analysis shows that the carbon is present as nanosized SiC. Parallel EELS analysis shows that the SiC has a nitrogen content of 2.3 wt%, based upon SiC weight.

Example 96

Repeat Example 95, but eliminate the Si_3N_4 powder used as a seed and decrease the reaction temperature from 1500°C to 1485°C. The resulting powder has a carbon content of 1.1 wt% (3.7 wt% as SiC), based upon powder weight. TEM analysis shows that the carbon is present as nanosized SiC. Parallel EELS analysis shows that the SiC has a nitrogen content of 9.9 wt%, based upon SiC weight.

Examples 95 and 96 demonstrate that composite powders of the invention contain SiC and that the SiC contains nitrogen. Similar results are expected with the composite powders of the other examples as well as with other composite powders prepared as described herein. By way of contrast, parallel EELS analysis of commercially available silicon carbide powder reveals no detectable level of nitrogen even after the powder has been subjected to a three hour heat treatment at 700°C in any one of air, nitrogen or a 50/50 (by volume) air/nitrogen mixture.

WHAT IS CLAIMED IS:

1. A process for preparing a silicon nitride-silicon carbide composite powder, the silicon carbide portion containing nitrogen, which comprises heating an admixture that comprises crystalline silica powder, carbon powder, and, optionally, crystalline silicon nitride powder to a temperature of from 1350°C to 1600°C in the presence of a nitrogen-containing atmosphere for a period of time sufficient to convert the admixture to a composite α-silicon nitride/silicon carbide powder, the silicon carbide portion of the powder having a mean number diameter within a range of from 10 to 700 nanometers and containing an amount of nitrogen, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion.

2. The process of Claim 1, wherein the nitrogen-containing atmosphere is established by gaseous nitrogen, gaseous ammonia, gaseous mixtures of nitrogen and ammonia, gaseous mixtures of nitrogen, ammonia or both with an inert or noble gas, or gaseous mixtures of nitrogen, ammonia or both with hydrogen and, optionally, an inert or noble gas.

3. The process of Claim 1, wherein the nitrogen-containing atmosphere is flowing.

4. The process of Claim 1, wherein, prior to heating to the temperature of from 1350°C to 1600°C, the admixture is blended with a binder composition and formed into shaped masses of material that are then converted to calcined masses by heating them to a temperature sufficient to decompose components of the binder composition into a solid carbonaceous residue and maintaining that temperature until evolution of residual gases effectively ceases, the calcined masses having a carbon content that is greater than stoichiometrically required to reduce the silica via carbothermal reduction.

5. The process of Claim 4, wherein preparation of the composite α-silicon nitride/silicon carbide powder is represented by an equation:

$$3\,SiO_2 + (6+x)C + 2N_2 + y\,Si_3N_4 = (1+y)\,Si_3N_4 + 6\,CO + xC$$

where x is a real number within a range of from greater than 0 to 18 and y is a real number within a range of from 0 to 1.28.

6. The process of Claim 5, wherein y is a real number within a range of from 0.2 to 0.8.

7. The process of Claim 5, wherein x is a real number within a range of from 0.6 to 12.

8. The process of Claim 1, further comprising a sequential step wherein the composite α-silicon nitride/silicon carbide powder is heated to a temperature within a range of from 500°C to 1000°C in an oxidizing atmosphere for a period of time sufficient to effect removal of excess free carbon.

9. The process of Claim 8, wherein, after removal of excess free carbon, the composite powder has a silicon nitride phase that is at least 90 percent by weight, based upon silicon nitride phase weight, α-silicon nitride and a silicon carbide phase that is in the form of particles having a mean number diameter within a range of from 10 to 700 nanometers, the silicon carbide phase being present in an amount of from greater than 0 to 50 percent by weight, based upon composite powder weight, and containing an amount of nitrogen, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion, the composite powder having a BET surface area of from 3 to 15 m^2/g.

10. The process of Claim 4, wherein the binder is a combination of a first reactant selected from the group consisting of monosaccharides, disaccharides, polysaccharides, starches, modified starches, soy protein, cellulose ethers and cellulose ether derivatives and at least one second reactant having at least one reactive nitrogen-containing moiety.

11. The process of Claim 10, wherein the binder is a combination of sucrose and melamine.

12. The process of Claim 1, wherein heating to the temperature of from 1350°C to 1600°C occurs first at a temperature less than 1500°C for a first period of time and then at a second temperature of at least 1500°C for a second period of time that is shorter than the first period of time, and the silicon carbide portion of the composite powder is present as a bimodal distribution as determined by transmission electron microscopy.

13. The process of Claim 12, wherein the first period of time is from 120 to 470 minutes, the first temperature is from 1425 to 1490°C, the second period of time is from 10 to 120 minutes, and the second temperature is from 1500 to 1600°C.

14. The process of Claim 12, wherein the bimodal distribution has a first distribution peak located at a mean number diameter within a range of from 10 to 200 nanometers and a second distribution peak located at a mean number diameter within a range of from 200 to 700 nanometers.

15. The process of Claim 1, wherein heating to the temperature of from 1350°C to 1600°C occurs at an initial temperature that thermodynamically favors formation of SiC over formation of Si_3N_4 for a first period of time to generate submicrometer SiC crystallites and then at a second temperature that favors formation of Si_3N_4 over SiC for a second period of time that is longer than the first period of time.

16. The process of Claim 15, wherein the initial temperature and the first period of time are sufficient to provide the composite powder with a SiC content that is greater than 0 wt%, but less than about 50 wt%, based upon composite powder weight, the SiC being in the form of crystallites having a mean number diameter that ranges from 10 nanometers to 700 nanometers.

17. The process of Claim 15, wherein the initial temperature is within a range of 1500-1550°C and the first period of time is from 1 minute to 45 minutes.

18. The process of Claim 1, wherein the admixture contains crystalline silicon nitride powder, the silica powder in the admixture has a purity of at least 99.5 percent and the carbon powder in the admixture has a purity of greater than 96 percent.

19. The process of Claim 18, wherein the silica powder is a crystalline quartz powder having a surface area greater than 0.2 square meters per gram and a mean particle diameter (d_{50}) less than 15 micrometers.

20. The process of Claim 18, wherein the carbon powder has a surface area of at least 20 square meters per gram and an average particle size of less than 0.10 micrometer.

21. The process of Claim 18, wherein the crystalline silicon nitride powder in the admixture has an alpha-silicon nitride content of at least 95 percent by weight, based upon weight of silicon nitride, a crystallite mean number diameter of less than about 0.2 micrometer, a surface area of at least about 7.5 m^2/g and a mean particle size (d_{50}) as determined by laser light scattering of less than about 1 micrometer.

22. The process of Claim 21, wherein the crystalline silicon nitride powder in the admixture is present in an amount sufficient to provide a ratio of silicon nitride powder as seed to silicon dioxide that is from 0.05:1 to 1:1.

23. The process of Claim 21, wherein the seed to silicon dioxide ratio is about 0.2:1.

24. The process of Claim 21, wherein the silicon nitride powder is a carbothermally synthesized material having a silicon carbide content of less than about 1.5 percent by weight and a silicon dioxide content of less than about 10 percent by weight, both percentages being based upon silicon nitride powder weight.

25. The process of Claim 18, wherein the crystalline silicon nitride powder in the admixture has a β-Si_3N_4 content of at least 75 wt%.

26. The process of Claim 18, wherein the silica powder is a crystalline quartz powder having a surface area of greater than 1.9 m^2/g and the composite α-silicon nitride/silicon carbide powder is substantially free of α-Si_3N_4 crystallites having β-Si_3N_4 fibers protruding therefrom.

27. The process of Claim 8, further comprising a step, subsequent to removal of excess carbon, wherein the composite α-silicon nitride/silicon carbide powder is subjected to a post synthesis heat treatment in the presence of nitrogen, an inert gas or a mixture thereof, at a temperature within a range of from 1400°C to 1500°C in for a period of time sufficient to cause at least a portion of residual silicon dioxide to react with at least a portion of the silicon carbide thereby resulting in a composite powder with an increased silicon nitride content relative to the composite powder prior to the post synthesis heat treatment.

28. The process of Claim 27, wherein the nitrogen, inert gas or mixture thereof is flowing

29. The process of Claim 27, wherein the period of time ranges from more than about five minutes to at least about 24 hours.

30. The process of Claim 27, wherein the period of time falls within a range of from 4 hours to 12 hours.

31. The process of Claim 1, wherein the admixture further comprises silicon metal powder in an amount sufficient to provide a ratio of silicon metal powder to silicon dioxide powder that falls within a range of from 0.05:1 to 1:1.

32. The process of Claim 31 wherein the range is from 0.1:1 to 0.5:1.

33. A silicon nitride-silicon carbide composite powder comprising a silicon nitride phase that is at least 90 percent by weight, based upon silicon nitride phase weight, α-silicon nitride and a silicon carbide phase that is in the form of particles having a mean number diameter within a range of from 10 to 700 nanometers, the silicon carbide phase having a nitrogen content, as determined by parallel electron energy loss spectroscopy, within a range of from 2 to 10 percent by weight of the silicon carbide portion, the silicon carbide phase being present in an amount within a range of from greater than 0 percent by weight to 50 percent by weight, based upon composite powder weight, the composite powder having a BET surface area of from 3 to 15 m^2/g.

34. The composite powder of Claim 33 having a silicon nitride crystallite mean number diameter of less than 0.3 μm, a surface area that lies within a range of from 8 to 13 m^2/g, and a mean number diameter for silicon carbide of less than 100 nanometers, less than 2 wt% residual oxygen as monatomic oxygen, and residual elemental impurities of less than 100 ppm calcium, less than 50 ppm iron, less than 200 ppm aluminum, less than 20 ppm sulfur, less than 50 ppm fluorine, less than 10 ppm potassium and less than 10 ppm chlorine and is substantially free of α-Si_3N_4 crystallites having β-Si_3N_4 fibers protruding therefrom.

35. The composite powder of Claim 33, wherein the silicon carbide phase is in the form of particles having a bimodal distribution, the bimodal distribution having a first distribution peak located at a mean number diameter within a range of from 10 to 200 nanometers and a second distribution peak located at a mean number diameter within a range of from 200 to 700 nanometers.

36. A silicon nitride-silicon carbide composite powder having a silicon nitride phase and a silicon carbide phase, the silicon nitride phase having a phase purity of >10% β-Si_3N_4 and comprising rod-like β-Si_3N_4 crystallites that have a mean number diameter of about 0.04 μm, the number diameter ranging from 0.01 to 0.10 μm, and a mean aspect ratio of from 5/1 to 8/1, ranging from 1.5/1 to 21/1 and α-Si_3N_4 crystallites that have a mean number diameter of from 0.1 to 0.2 μm, the number diameter ranging from 0.03 to 0.5 μm.

37. A process for preparing a self-reinforced silicon nitride ceramic body which comprises subjecting a powdered admixture of a carbothermally synthesized silicon nitride/silicon carbide composite powder, a densification aid, a conversion aid, at least one whisker growth enhancing aid and, optionally, a catalyst to conditions of temperature and pressure sufficient to yield a ceramic body having a density of at least 96 percent of theoretical density and form, in situ, β-silicon nitride whiskers having an average aspect ratio of at least 2.5, the body having both a granular and an intragranular distribution of residual silicon carbide grains and a fracture toughness of at least 7 $MPa \cdot m^{1/2}$, the intragranular silicon carbide grains having a mean number diameter within a range of from 10 to 400 nanometers, at least a portion of the intragranular silicon carbide grains containing nitrogen, as determined by parallel electron energy loss spectroscopy, in an amount that is within a range of from 2 to 10 percent by weight of the silicon carbide.

38. The process of Claim 37, wherein the powdered admixture is converted to a shaped body prior to being subjected to the conditions of temperature and pressure.

39. The process of Claim 37, wherein the body has a creep resistance that is greater than that obtained by substituting silicon nitride for the silicon nitride/silicon carbide composite powder.

40. The process of Claim 37, wherein the composite powder has a silicon carbide content that is within a range of from greater than zero percent by weight to 50 percent by weight, based upon composite powder weight.

41. A self-reinforced silicon nitride/silicon carbide ceramic body having a density of at least 96 percent of theoretical density and comprising a crystalline phase of β-silicon nitride of which at least about 20 volume percent, as measured by viewing one plane of the body by scanning electron microscopy, is in the form of whiskers having an average aspect ratio of at least 2.5 and a glassy grain boundary phase in an amount not greater than 35 percent by weight of total body weight, the silicon carbide being distributed, with respect to the β-silicon nitride whiskers, as granular and intragranular submicrometer grains, the body having a fracture toughness of at least 7 $MPa \cdot m^{1/2}$, the intragranular silicon carbide grains having a mean number diameter within a range of from 10 to 400 nanometers, at least a portion of the intragranular silicon carbide grains containing nitrogen, as determined by parallel electron energy loss spectroscopy, in an amount that is within a range of from 2 to 10 percent by weight of the silicon carbide.

42. The ceramic body of Claim 41, wherein the silicon carbide is present in an amount that is within a range of from greater than zero percent by weight to 50 percent by weight, based upon combined weight of silicon nitride and silicon carbide.

INTERNATIONAL SEARCH REPORT

Interna .l Application No
PCT/US 95/04573

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B35/584 C04B35/593 C01B21/068

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE EUROPEAN CERAMIC SOCIETY, vol.9, 1992, GB pages 219 - 230 T. LICKO ET AL. 'Synthesis of silicon nitride ...'	1-3,33, 34
A	see abstract see page 222 - page 224	4-9, 18-24, 26,31,32
A	EP,A,0 471 568 (THE DOW CHEMICAL COMPANY) 19 February 1992 cited in the application see claims 1,14	37,38,41

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
18 July 1995	28. 07. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Hauck, H

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INTERNATIONAL SEARCH REPORT

Interna :l Application No
PCT/US 95/04573

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,89 07093 (THE DOW CHEMICAL COMPANY) 10 August 1989 cited in the application see claims 1,18,22 -----	37,38,41

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 95/04573

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