PRECERAMIC COMPOSITIONS AND CERAMIC PRODUCTS

This application is a division of application Ser. No. 120,102, filed Nov. 13, 1987, now U.S. Pat. No. 4,835,207.

FIELD OF INVENTION

This invention relates to improved silicon carbide (SiC) ceramics, i.e., ceramics composed predominantly of SiC, and to preceramic compositions and processes for preparing them.

BACKGROUND

As disclosed in U.S. Pat. Nos. 4,117,057 (Yajima et al.) and 4,560,526 (Okumura et al.), it is known that ceramics can be prepared from mixtures of SiC powder and a preceramic binder and that the strengths of the ceramics decrease with decreasing density. An unfortunate result of this strength/density relationship is that ceramics having typical densities (i.e., about 2.0–2.5 g/cc) have generally not been obtainable with ufficiently high bending strengths (i.e., at least about 20, preferably at least about 28 kg/mm^2) to make them commercially attractive.

A Shin Nisso Kako Co., Ltd. product specification sheet, "SiC Products by PPMC Process," indicates that ceramics having a density of 2.3 g/cc and bending strengths of 20–30 kg/mm^2 can be obtained from a mixture of SiC powder, polysilastyrene, and an organic lubricant. However, independent measurements of disc specimens provided by Shin Nisso show the bending strengths of these ceramics to be only about 18–21 kg/mm^2 and the specific strengths, i.e., the bending strength/density ratios, to be only about 9.6–11.1 (kg/mm^2)/(g/cc). This represents an improvement over the strengths of previously known low density SiC ceramics but not as much of an improvement as might be desired.

U.S. Pat. Nos. 4,482,669 (Seyferth et al. A), 4,645,807 (Seyferth et al. B), 4,650,837 (Seyferth et al. C), and 4,659,850 (Arai et al.) disclose the utility of polysilazanes as preceramic materials, and Seyferth et al. A teach that their polysilazanes -are especially useful as binders for ceramic powders such as SiC. SiC ceramics prepared from these SiC powder/polysilazane binder compositions are composed predominantly of SiC, e.g., about 80–90% SiC, with the balance being mostly silicon nitride. Seyferth et al. A do not disclose the typical densities and bending strengths of ceramics made from their preceramic compositions. However, Wiseman, "The Development and Application of Polysilazane Precursors to Ceramics,+ a Massachusetts Institute of Technology thesis, 1984, shows that these densities were generally about 2.0–2.4 g/cc and the bending strengths were poor. Wiseman shows a recognition, though, of its being desirable to minimize alkali metal contamination and to use preceramic polymers having a sufficiently high molecular weight, or mixtures (such as 80/20 mixtures) of such polymers with lower molecular weight polymers, to maximize strength.

SUMMARY OF INVENTION

An object of this invention is to provide novel preceramic polysilazane compositions capable of forming high strength/low density SiC ceramics.

Another object is to provide processes for preparing such compositions and converting them into high strength/low density SiC ceramics.

A further object is to provide novel high strength/-low density SiC ceramics.

These and other objects are attained by (A) intimately mixing about 50–85% by weight of SiC powder with about 15–50% by weight of a preceramic polysilazane binder, (B) pulverizing the mixture to form particles having a particle size smaller than 105 micrometers, i.e., particles which pass through a 105 micrometer sieve, (C) separating from those particles any particles having a particle size larger than about 105 micrometers, i.e., particles which are retained on a 105 micrometer sieve, (D) molding the resultant composition having a particle size not larger than about 105 micrometers, and (E) pyrolyzing the molded composition in an inert atmosphere to a temperature of about 1200°–1450° C. Detailed Description.

SiC powders that can be employed in the practice of the invention are commercially-available materials that vary from very fine to coarse powders. However, the preferred SiC powders are those which have a particle size of about five micrometers or less, preferably one micrometer or less; and particularly good results have been obtained with SiC powders having a substantially spherical particle shape and mean particle sizes of about 0.2–5.0 micrometers, preferably 0.2–1.0 micrometer. Both alpha-SiC and beta-SiC are utilizable.

The binder that is mixed with the SiC powder is a polysilazane, e.g., the polysilazanes of Seyferth et al. A, B, and C, and Arai et al., the teachings of all of which are incorporated herein in toto by reference. It is preferably a polysilazane of the type taught by Seyferth et al. A, i.e., a polysilazane prepared by reacting an organodihalosilane with ammonia, treating the ammonolysis product with a basic catalyst which is capable of quenching the resultant product with an electrophilic quenching reagent, or a mixture of such polysilazanes. For example, it may be one or more polysilazanes prepared by reacting methyldichlorosilane with ammonia, treating the ammonolysis product with KH, and quenching the resultant product with methyl iodide or dimethylchlorosilane. The utilizable polysilazanes are solids which are soluble in common organic solvents, such as aliphatic or aromatic hydrocarbons, dialkyl or alicyclic ethers, etc., including solid mixtures of normally solid polysilazanes and normally liquid polysilazanes. The solid, soluble polysilazanes having the higher molecular weights are preferred to permit the use of faster pyrolysis rates.

When good strength retention at elevated temperatures is desired, the polysilazane that is utilized should have an alkali metal content not higher than about 100 ppm, preferably not higher than about 5 ppm. When the polymer as prepared contains more than that amount of alkali metal contaminant, the degree of contamination can be reduced in any suitable manner, such as by filtration of a solution of the polysilazane in an organic solvent.

The amount of polysilazane used is such that the preceramic composition comprises about 50–85% by weight of SiC powder and about 15–50% by weight of binder, preferably about 70–80% by weight of SiC powder and about 20–30% by weight of binder.

If desired, the compositions may be modified by the inclusion of optional ingredients, such as polyisobutenyl succinimides, other dispersing agents, and other addi-