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(72) Inventeurs/Inventors:
MATSUMOTO, ROGER L. K., US;
SCHWARK, JOANNE M., US

(73) Propriétaire/Owner:
KION CORPORATION, US

(74) Agent: ROGERS LAW OFFICE

(54) Titre : POLYMERES PRECERAMIQUES COMPRENANT DU BORE
(54) Title: PRECERAMIC POLYMERS INCORPORATING BORON

(57) Abrégé/Abstract:
A boron-substituted polysilazane in which the boron is derived from a borane and is bound to the polysilazane through boron-carbon bonds is disclosed. The polysilazane is prepared by reacting a silazane ammonolysis product containing at least one 2-6 carbon alkenyl or alkenyl group with a borane containing at least one B-H group per molecule. The boron-substituted polysilazane can be used to prepare silicon carbide-containing ceramic articles.

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Matsumoto & Schwark Case 1

Preceramic Polymers Incorporating Boron and Their Application in the Sintering of Silicon Carbide Ceramics

Abstract of the Disclosure

A boron-substituted polysilazane in which the boron is derived from a borane and is bound to the polysilazane through boron-carbon bonds is disclosed. The polysilazane is prepared by reacting a silazane ammonolysis product containing at least one 2-6 carbon alkenyl or alkenyl group with a borane containing at least one B-H group per molecule. The boron-substituted polysilazane can be used to prepare silicon carbide-containing ceramic articles.

The present invention relates to boron-substituted polysilazanes.

Silicon carbide is a structural ceramic with good high temperature properties. Like other covalently bonded ceramics, such as silicon nitride, silicon carbide must be sintered with the addition of sintering aids. Sintering aids help to form a coherent bonded mass by mechanisms such as the formation of liquid phases or by enhancing solid state diffusion through the bulk or on the surface of the powdered particles. Unlike silicon nitride, which must be sintered via liquid phase sintering due to the decomposition of Si_3N_4 that occurs at 1800°C, silicon carbide is sintered via surface diffusion at 2100°C. Silicon nitride, therefore, has poor high temperature properties due to the glassy intergranular phase. Silicon carbide, in contrast, maintains its properties to high temperature without degradation because there is no intergranular glassy phase that can soften. While it is possible to sinter silicon carbide via liquid phase sintering, the result would not be a useful high temperature ceramic.

Silicon carbide is currently sintered with boron and carbon, or aluminum and carbon additives. These additives increase the surface diffusion of silicon carbide.

Prochazka, et al. (J. Am. Ceram. Soc. 1985, 68(9)479), found that SiC could be sintered to 97% of theoretical density at 2100°C with the addition of 0.5 wt. % B and 1.5 wt. % C. In this case, the boron must be well distributed throughout the powder and the carbon must be amorphous. These additives were introduced into the SiC powder by ball milling a mixture of the SiC powder with elemental boron or boron carbide for two hours in hexane. This traditional milling technique provides macroscopic mixing of the sintering aids throughout the bulk powder. Since the boron and carbon are added separately, however, regions that are rich in boron or carbon may be formed.

Although polysilazanes containing boron have been disclosed, these polysilazanes have been prepared by methods that introduce boron-nitrogen or boron-oxygen bonds into the polysilazanes. For example, the Niebylski patents U.S. 4,910,173; 4,921,925 and 5,045,399 describe the reaction of trialkylboroxine, triaryloxyboroxine, or trialkoxyboroxine with a polysilazane to form an organoborosilazane polymer. However, the boron in these polymers is not bound to the polysilazane through boron-carbon bonds.

The boron-substituted polysilazane composition of this invention is characterized in that the boron is derived from a borane and is bound to the polysilazane through boron-carbon bonds.

Also according to the invention, the boron-substituted polysilazanes are prepared by reacting ammonia with a halogenated silicon compound containing at least one 2-6

carbon alkenyl or alkynyl group to form a silazane ammonolysis product, and reacting the ammonolysis product with a borane containing at least one B-H group per molecule.

Also according to the invention, the boron-substituted polysilazanes can be pyrolyzed to form an amorphous char that contains boron homogeneously distributed on a molecular level. The char can be used as a sintering aid in the manufacture of SiC ceramic articles.

The problems encountered in previous attempts to uniformly disperse sintering aids in silicon carbide powders can be overcome by using the boron-substituted polysilazanes of this invention as binders. The boron is bound through boron-carbon bonds to the polysilazane backbone, resulting in uniform distribution of the boron upon pyrolysis of the polymer.

In accordance with the present invention, a preceramic polymer, also referred to as a polymer precursor, containing boron-carbon bonds is prepared by the hydroboration of alkenyl- or alkynyl-substituted silicon compounds. Although hydroboration reactions are preferred for this purpose, other procedures that incorporate B-C moieties into the preceramic polymer can also be used.

The silicon compounds used to form the boron-substituted preceramic polymers of the present invention are preferably selected from polysilanes, polysilazanes, polycarbosilanes, or any monomeric or oligomeric silicon compound that has appropriate unsaturated substituents for

hydroboration and, upon pyrolysis at a temperature of at least 800°C under an inert atmosphere forms an amorphous or crystalline ceramic char containing boron, silicon and carbon. Polysilazanes are most preferred.

Suitable polysilanes for purposes of the present invention include, for example, $[(MeSiH)(MeSiCH=CHPh)_m]_n$, and $[(MeSiH)(MeSiCPh=CH_2)_m]_n$, (Du. Z.; Qui, H. J., Poly. Sci.: Part A: Poly. Chem., 1989, 27, 2861-2869); $[(Me_3Si)(Me_2Si)_x(MeSiCH=CH_2)_y(SiMe_3)]_m$ (Schilling, C.L., Jr., British Poly. J., 1986, 18(6), 355-58); and $[(MeSiH)_x(MeSiCH=CH_2)_y]_z$ (Union Carbide vinylpolysilane Y-12044).

Suitable polycarbosilanes include, for example, $[Me_2Si-C\equiv C-]_n$ $[Ph_2Si-C\equiv C]_n$, $[PhMeSi-C\equiv C]_n$ and $[Me_2SiMe_2Si-C\equiv C]_n$ as disclosed by T.J. Barton et al. in U.S. Patent No. 4,940,767.

While polysilanes and polycarbosilanes containing appropriate substituents such as those listed above can be used in this invention, the following discussion and the examples presented below use hydroborated polysilazanes.

Polysilazane is meant to include cyclic oligomers and ring-based and linear polymers. The first step of the preferred process for preparing the boron-substituted polysilazanes is an ammonolysis reaction that involves reacting ammonia, or a mixture of ammonia and a substituted or unsubstituted 1-4 carbon alkyl or aryl amine, with a halogenated silicon compound selected from $RSiX_3$, $RR'SiX_2$ and mixtures thereof, including mixtures where more than one

compound having the formula $RSiX_3$ or $RR'SiX_2$ is used. Optionally, $RR'R''SiX$, SiX_4 or mixtures thereof can also be present in the reaction mixture. X can be Cl, Br or I. Cl is preferred. R, R', R'' can be the same or different and are selected from the group consisting of H, substituted or unsubstituted 1-6 carbon alkyl, aryl, 2-6 carbon alkenyl and 2-6 carbon alkynyl groups. Standard ammonolysis procedures, such as those described in U.S. Patent No. 4,929,704, can be used.

The ammonolysis reaction mixture must contain at least one halogenated silicon compound having an alkenyl or alkynyl group that can take part in the hydroboration reaction. Examples of suitable halogenated silicon compounds include, for example, methyldichlorosilane, vinylmethyldichlorosilane, tetrachlorosilane, tetrabromosilane, trichlorosilane, vinyltrichlorosilane, methyltrichlorosilane, phenyltrichlorosilane, ethyltrichlorosilane, propyltrichlorosilane, butyltrichlorosilane, methyltribromosilane, dimethyldichlorosilane, phenylmethyldichlorosilane, dimethyldibromosilane, trimethylchlorosilane, dimethylchlorosilane, dimethylvinylchlorosilane, phenylvinyldichlorosilane, allylmethyldichlorosilane, allyltrichlorosilane, 4-but-1-enyldichloromethylsilane and trimethylbromosilane. Preferred alkenyl chlorosilanes are methylvinyldichlorosilane, vinyltrichlorosilane, dimethylvinylchlorosilane, phenylvinyldichlorosilane,

allylmethyldichlorosilane, allyltrichlorosilane, and 4-but-1-enyldichloromethylsilane.

The ammonolysis product, when ammonia alone is reacted with the halogenated silicon compound, is predominantly a mixture of cyclic compounds of varying ring size, but can possibly contain small amounts, usually less than 1%, of linear species. When a mixture of ammonia and an alkyl or aryl amine is used, the ammonolysis product contains more linear than cyclic species.

The resultant alkenyl- or alkynyl-substituted polysilazane, in which the sites of alkenyl or alkynyl unsaturation are directly bound to the silicon in the polysilazane, is then reacted with a borane containing at least one B-H bond per molecule. Any borane containing at least one B-H bond/molecule can be used. Boranes suitable for use in this invention can be selected from RR'BH, RBH_2, and $BH_3 \cdot L$ in which R and R' are the same or different and are selected from the group consisting of 1-10 carbon alkyl groups, aryl groups, 2-6 carbon alkenyl groups, and 2-6 carbon alkynyl groups and L is a Lewis base donor. Typical Lewis bases include, for example, pyridine, ammonia, t-butylamine, dimethylamine, methyl sulfide and trimethylamine. Thus, suitable boranes include, for example, decaborane, pentaborane, diborane, borane-ammonia complex, borane-tert-butylamine complex, borane-N,N-diethylaniline complex, borane-N,N-diisopropylethylamine complex, borane-dimethylamine complex, 4-(borane-dimethylamino)pyridine complex, borane-4-ethylmorpholine

complex, borane-2,6-lutidine complex, borane-4-methylmorpholine complex, borane-methyl sulfide complex, borane-morpholine complex, borane-1,4-oxathiane complex, borane-4-phenylmorpholine complex, borane-piperazine complex, borane-piperidine complex, borane-poly(2-vinylpyridine) complex, borane-pyridine complex, borane-trimethylamine complex, borane-triphenylphosphine complex, 9-borabicyclo[3.3.1]nonane, dicyclohexylborane, bis-3-methyl-2-butylborane, sym-bis(2,4,4-trimethyl-3-pentyl)diborane, sym-tetrakis-(trans-2-methylcyclohexyl)-diborane and sym-tetraisopinocampheyldiborane. The most preferred borane is dicyclohexylborane.

The hydroboration reaction, which is the preferred means for incorporating B-C moieties into the preceramic polymer, can be carried out over a wide range of temperatures, e.g., from -78°C to 200°C, depending upon the specific organosilicon compound and borane chosen. The preferred reaction temperature range is from -78°C to 30°C. The reaction can be conducted with or without a solvent, although it is preferably conducted with a solvent. Solvents such as tetrahydrofuran, toluene, diethyl ether and dichloromethane can be used, provided the B-H containing compound is compatible with the solvent. Typical reaction conditions and examples of hydroboration reactions are well known, for example, as disclosed by Brown, H.C. "Hydroboration"; W.A. Benjamin, Inc.: New York, 1962, and Brown, H.C., Curr. Trends Org. Synth. Proc. Int. Conf., 4th 1982, 247-68. The boron-substituted polysilazane products

typically contain at least a small amount of unsaturation, although it is possible for all of the unsaturated groups to react in the hydroboration reaction.

The boron-substituted polymers prepared in accordance with the present invention can be in the liquid, solid, or fusible state. For fusible precursors, i.e., liquids, and soluble and/or meltable solids, that contain residual alkenyl or alkynyl substituents, further crosslinking can be introduced into the material by a thermosetting process in which the polymer is heated in the presence of a free radical generator. An effective quantity of a free radical generator means a quantity sufficient to crosslink the boron-substituted polysilazane. The concentration of the free radical generator is generally from 0.01 to 5.0 wt.% based on the weight of the polysilazane. The thermosetting reaction is conducted at a temperature at which a significant fraction of the free radical generator has decomposed to form radical species. This temperature will depend upon the particular free radical generator chosen and can be readily determined by one skilled in the art. For example, when 0.5 wt. % of the free radical generator dicumyl peroxide is used, the thermosetting reaction takes place readily at 130°C. Higher or lower thermosetting temperatures can be needed depending upon the free radical generator chosen.

For purposes of the present invention, free radical generators include, for example, peroxides and azo compounds. Suitable peroxides include dicumyl peroxide, t-

butyl cumyl peroxide, bis-2,4-dichlorobenzoyl peroxide, t-butyl perbenzoate, t-butyl peracetate, 2,5-di(t-butylperoxy)hexane, and di-t-butyl peroxide. Suitable azo compounds include 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), and 2-(t-butylazo)isobutyronitrile. The boron-substituted polymers can also be cured by exposure to UV light, gamma rays or electron beam irradiation.

A specific application for which the polymers of the present invention are particularly suited is the sintering and subsequent densification of silicon carbide, wherein good dispersion of sintering aids in the SiC powder is necessary to produce a uniform ceramic article. Three routes to a SiC-containing ceramic are possible: i) pyrolysis of the unfilled polymer; ii) pyrolysis of the polymer with fillers other than SiC; and iii) in the preferred embodiment, pyrolysis of the polymer in which the filler is substantially SiC.

The unfilled polymers of this invention, under the appropriate pyrolysis conditions, can be converted to monolithic sintered silicon carbide articles provided they contain an amount of boron sufficient to promote sintering of the SiC formed in the pyrolysis of the polymer. From 0.1 to 20 wt. % boron in the preceramic polymer is preferred, with 0.2 to 2.0 wt. % boron being more preferred, and 0.3 to 1.0 wt. % being most preferred.

The boron-substituted, preceramic polymers of the present invention can further contain ceramic or metal

fillers other than SiC including, e.g., Si, Si_3N_4, SiO_2, AlN, BN, Al_2O_3, TiN, TiC, Ti, Zr, Hf, ZrO_2, Y_2O_3, B_4C and ZrC in the form of powders, whiskers, or platelets. When such fillers are used, they can be present in an amount such that after sintering no more than 50 wt. % of the total sintered article comprises the filler.

In a preferred embodiment of this invention, SiC is used as a filler in the boron-substituted preceramic polymers and can be present in an amount of from 10 wt. % to 98 wt. % of the total precursor/SiC mixture. α-SiC, ß-SiC, and mixtures thereof can be used. Additionally, mixtures of the boron-substituted preceramic polymer with SiC and other ceramic or metal fillers can be used. When present, the SiC and other ceramic or metal fillers must provide enough SiC so that the sintered article contains at least 50 wt. % SiC.

Mixtures of SiC powder and/or additional fillers with the boron-substituted polysilazanes of this invention can be prepared using standard ceramic mixing equipment including, for example, a ball mill, a double planetary mixer, a three roll mill, a sigma blade mixer, a ribbon blender, an extruder and other methods known to those skilled in the art.

Mixtures of the boron-substituted polysilazane binder and fillers can be molded by processes including, for example, dry pressing, tape casting, isostatic pressing, extrusion and injection molding. Because each of these molding operations requires a different amount of boron-substituted polymer, the amount of boron present in the

polymer can be tailored so that the overall boron content of the system, i.e., the preceramic polymer binder, SiC powder and other fillers, is appropriate to sinter the silicon carbide.

For example, injection molding requires 15 wt. % to 50 wt. % polymer, while extrusion uses 30 wt. % to 60 wt. % polymer. If the total system boron content for sintering each molding mixture, i.e., polymer, SiC, and/or additional fillers, was set at 0.5 wt. %, for example, the polymer used in injection molding would require a higher boron substitution content than that used for extrusion, since less polymer is used in the injection molding process. Thus, a 0.5 wt. % boron level in an injection molding mix containing 30 wt. % preceramic polymer, which provides a 50 wt. % char at 1400°C, would require a boron level of 1.4 wt. % in the boron-substituted polysilazane. Likewise, a 0.5 wt. % boron level in an extrusion mix containing 50 wt. % preceramic polymer, which provides a 50 wt. % char at 1400°C, would require a boron level of 0.7 wt. % in the boron-substituted polysilazane.

Silicon carbide can be consolidated with a boron-containing amorphous char by a process that involves heating a mixture of silicon carbide and the boron-substituted silicon polymer of this invention under pyrolysis conditions at a temperature and for a time sufficient to produce a sintered silicon carbide article having a substantially homogeneous distribution of boron on a molecular level throughout the silicon carbide. When the preceramic polymer

is a liquid or soluble solid, the SiC is uniformly coated with the polymer, in contrast to previous work with sintering aids for SiC in which the boron is added as discrete particulates of B or B_4C. Since the polymers of the present invention have a homogeneous distribution of boron and carbon in the polymer and also in the char produced by pyrolysis of the polymer, the char is effective for sintering silicon carbide. This provides a homogeneous distribution of both boron and carbon throughout the molded SiC article. In addition, the excess carbon in the char, as well as the silicon present, further combine to produce SiC and contribute to the overall compositional integrity of the fired ceramic body.

As used herein, sintering means the process in which two adjacent ceramic grains become physically connected. There have been many mechanisms postulated for this, not all of which result in densification. All sintering mechanisms rely upon movement of matter in order to connect adjacent grains. Densification means the increase of matter in a specific volume, or a decrease of the void space. Although often used synonymously, the terms sinter and densify, as found in this specification, have specific, and different, meanings.

Pyrolysis of the SiC/polymer mixture must be conducted in a non-reactive atmosphere, such as a nitrogen, argon, helium, hydrogen, or ammonia-containing atmosphere. Pyrolysis at temperatures of at least 800°C but less than 1400°C produces an amorphous boron-containing char from the

boron-substituted preceramic polymer. The char further contains carbon, silicon and nitrogen. The boron is not present as either elemental boron or boron carbide. Further heating, to temperatures of at least 1800°C, will crystallize the char. While not wishing to be bound by any particular theory, it is believed that sintering occurs during crystallization of the preceramic polymer because atomic mobilities are maximized. Since the temperature at which a specific boron-substituted polymer will crystallize during pyrolysis varies, the temperature required to sinter each SiC/polymer mixture will vary. Additional heating at temperatures greater than the crystallization temperature, i.e., to temperatures of at least 1900°C, may be required to fully densify the molded article. As used herein, "fully densify" means to attain a density that is 90% or greater of the theoretical density of single crystal silicon carbide.

The cured or uncured boron-substituted preceramic polymers can also be used in the preparation of ceramic fibers and foams, in the infiltration of a preform structure and subsequent pyrolysis to a ceramic composite, in the production of oxidation resistant coatings, as a thin film, and as an adhesive or sealant.

In the following examples, a variety of boron-substituted polysilazanes were prepared by reacting a vinyl-substituted polysilazane with varying levels of dicyclohexylborane. The reaction chemistry for preparing each precursor is shown in Schemes 1-3 below. Polymers I, II and III each contain different addition levels of boron.

EXAMPLE 1

Scheme 1 shows the reaction of a vinyl-substituted polysilazane with 8 mol % dicyclohexylborane. The liquid poly(methylvinyl)silazane was prepared by the ammonolysis of a mixture of methyldichlorosilane and methylvinyldichlorosilane (4:1 mole ratio). This precursor was then reacted with dicyclohexylborane [$(cy)_2BH$] generated by the reaction of two equivalents of cyclohexene with one equivalent of $BH_3 \bullet THF$ adduct. The reaction sequence is shown in Scheme 1.

Scheme 1

$$0.08\ BH_3 \bullet THF + 0.16\ \text{C}_6\text{H}_{10} \xrightarrow{0°C} 0.08\ (cy)_2BH$$

$$0.08\ (cy)_2BH + 1\ [(MeSiHNH)_{0.8}\ (MeSiCH{=}CH_2NH)_{0.2}]_x \xrightarrow{0°C} \xrightarrow{RT}$$

$$[(MeSiHNH)_{0.8}\ (MeSiCH{=}CH_2NH)_{0.12}\ (MeSiCH_2CH_2B(cy)_2NH)_{0.08}]_x$$

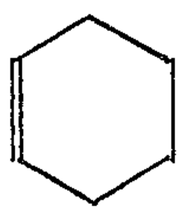
(Polymer I)

The product of hydroboration, designated Polymer I, contains 8 mol% boron. The formula representing Polymer I is written, for convenience only, as if the hydroboration occurred by ß-addition; α-addition products can also be present. Because Polymer I contains residual vinyl substituents, it can be thermoset by heating with a free radical generator, e.g., dicumyl peroxide, to 150°C.

EXAMPLE 2

The method used to prepare this boron-substituted polysilazane can be extended to many other preceramic polymer systems. Scheme 2 shows the hydroboration of an oligomeric methylvinylsilazane, $(MeSiCH{=}CH_2NH)_x$, to give Polymer II which contains 33 mol % boron.

Scheme 2

$$0.33\ BH_3{\bullet}THF + 0.66\ \text{  } \xrightarrow{0\,^\circ C} 0.33\ (cy)_2BH$$

$$0.33\ (cy)_2BH + 1\ (MeSiCH{=}CH_2NH)_x \xrightarrow{0\,^\circ C\ \ RT}$$

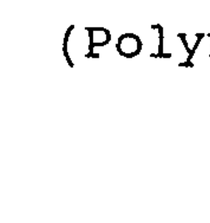
$$[(MeSiCH{=}CH_2NH)_{0.67}\ (MeSiCH_2CH_2B(cy)_2NH)_{0.33}]_x$$

(Polymer II)

EXAMPLE 3

Polymer III was generated by the hydroboration of the polysilazane $[(MeSiHNH)_{0.8}\ (MeSiCH{=}CH_2NH)_{0.2}]_x$ to give a polymer with 19 mol% boron. The reaction scheme is shown below.

Scheme 3

$$0.19\ BH_3{\bullet}THF + 0.38\ \text{  } \xrightarrow{0\,^\circ C} 0.19\ (cy)_2BH$$

$$0.19\ (cy)_2BH + 1\ [(MeSiHNH)_{0.8}\ (MeSiCH{=}CH_2NH)_{0.2}]_x \xrightarrow{0\,^\circ C\ \ RT}$$

$$[(MeSiHNH)_{0.8}\ (MeSiCH{=}CH_2NH)_{0.01}\ (MeSiCH_2CH_2B(cy)_2NH)_{0.19}]_x$$

(Polymer III)

EXAMPLES 4-15

The utility of the boron-substituted polymers of this invention is illustrated by the following Examples.

All reactions were conducted under nitrogen using standard inert atmosphere techniques. Solvents were dried with 4A and 13X Linde molecular sieves and sparged with dry nitrogen before use. Cyclohexene and 1.0 M borane-THF adduct were obtained from Aldrich and used as received. Dicumyl peroxide was obtained from the Hercules Gibbstown, New Jersey (U.S.A.) plant and used as received. Fine-grained Starck A-10 and B-10 silicon carbide powders were used in the sintering and densification studies.

For Examples 5 and 7, samples were pyrolyzed in an Astro Model 1000 furnace under an Ar atmosphere with a 10°C/min ramp and a maximum temperature of 1600°C. A one-hour hold at the maximum temperature was used. For Examples 9, 12, and 13, samples were hot-pressed at 280 kg/cm^2 (4000 psi) in a 5.1 cm (2") graphite die. The hot press used was a Thermal Technology Inc. Model HP 50-HTG-7010 with a graphite hot zone. The pressing schedule was 10°C/min to 2100°C with a 2 hour hold at a maximum temperature. Ceramic samples were characterized by X-ray powder diffraction and scanning electron microscopy (SEM). Densities were determined by geometrical measurement and calculation.

EXAMPLE 4

A 100 ml, three-necked, round-bottomed flask was sparged with nitrogen and equipped with a 25 ml dropping

funnel, a thermometer, a stir bar and a septum. The flask was charged with 13.0 ml (13.0 mmol) $BH_3 \cdot THF$ adduct and cooled to 0°C in an ice bath. The dropping funnel was charged with 2.64 ml (26.0 mmol) cyclohexene and 10 ml tetrahydrofuran (THF). The cyclohexene/THF mixture was added dropwise over 35 min. A white solid (dicyclohexylborane) formed. The reaction mixture was stirred for one hour at 0°C. The dropping funnel was then charged with 10.0 g (155.4 mmol) poly(methylvinyl)silazane, $[(MeSiHNH)_{0.8}\ (MeSiViNH)_{0.2}]_x$, and 10 ml THF and added to the reaction mixture over fifteen minutes. After the polysilazane addition was complete, the reaction mixture was stirred for 45 min at 0°C and then warmed to room temperature. The white solid disappeared and a clear solution was formed. The THF was removed in vacuo to give an opaque liquid with a viscosity of 402 centipoise (cps). The boron-substituted polysilazane, Polymer I, contained 1.1 wt. % boron bound to the polymer backbone. TGA analysis (10°C/min,25-950°C): 47.3 wt. %.

A one ounce jar was equipped with a stir bar and a septum, charged with 0.1 g dicumyl peroxide and sparged with nitrogen. Polymer I (5 g) was added by syringe. The jar, with a nitrogen inlet in the septum, was placed in a heated oil bath. At 150°C, the liquid cured (thermoset) and a solid formed. TGA analysis (10°C/min, 25-950°C): 63.2 wt. %.

For the hydroborated poly(methylvinyl)silazane described in Example 4, sintering was demonstrated on a

local scale at 1600°C, a temperature at which the boron-substituted preceramic polymer is partially crystallized. Complete densification of a SiC article containing the boron-substituted/substituted preceramic polymer binder was effected by hot pressing at 2100°C.

EXAMPLE 5

Under nitrogen, 70% by weight of Starck A-10 α-SiC powder was mixed into Polymer I containing 0.5 wt. % dicumyl peroxide. The mixture was cured by heating at 150°C under nitrogen. The cured piece was fired in a carbon crucible under an argon atmosphere at a ramp rate of 10°C/min to 1600°C. The furnace temperature was maintained at 1600°C for one hour after which the power was turned off and the sample was allowed to cool in the furnace. Examination of a fractured surface via SEM showed that the material had sintered. The fracture proceeded through the individual grains and the grains were approximately 3-5 μm in diameter.

EXAMPLE 6

For comparative purposes, a monolithic sample of a commercial α-silicon carbide ceramic was obtained from Hexoloy SA, Carborundum. The Hexoloy SA sample is an α-silicon carbide that is reportedly pressureless sintered at 2100°C. An SEM micrograph of a fracture surface shows some porosity. There is a strong similarity, however, of this micrograph to that of the pyrolyzed SiC-filled, boron-substituted polysilazane of Example 5. An equivalent

microstructure has thus been achieved at a firing temperature 500°C lower by using a boron-substituted polysilazane binder.

EXAMPLE 7

Starck A-10 α-SiC powder (70 wt. %) was mixed into poly(methylvinyl)silazane containing 0.5 wt. % dicumyl peroxide. The mixture was cured by heating under nitrogen at 150°C. The cured piece was fired in a carbon crucible under an argon atmosphere at a ramp rate of 10°C/min to 1600°C. The furnace temperature was maintained at 1600°C for one hour, after which the power was turned off and the sample was allowed to cool in the furnace. Examination of a fractured surface via a scanning electron microscope (SEM) showed that while there is some interconnectivity between the individual grains, the majority of the material is composed of loose particles. The fracture proceeded entirely between grains and the micrograph of the surface shows no apparent fracture patterns.

EXAMPLE 8

A 250 ml, three-necked, round-bottomed flask was sparged with nitrogen and equipped with a 50 ml dropping funnel, a thermometer, a stir bar, and a septum. The flask was charged with 46.25 ml (46.25 mmol) BH_3•THF adduct and cooled to 0°C in an ice bath. The dropping funnel was then charged with 9.37 ml (92.5 mmol) cyclohexene and 36 ml tetrahydrofuran (THF). The cyclohexene/THF mixture was

added dropwise over 45 min. A white solid (dicyclohexylborane) formed. The reaction mixture was stirred for one hour at 0°C. The dropping funnel was then charged with 11.76 g (138 mmol) methylvinylsilazane, $(MeSiViNH)_x$ and 36 ml THF and added to the reaction mixture over thirty minutes. After the polysilazane addition was complete, the reaction mixture was stirred for 45 minutes at 0°C and then warmed to room temperature. The white solid had disappeared and a clear solution was formed. The boron-substituted polysilazane, Polymer II, contained 2.5 wt. % boron bound to the polymer backbone. This solution was used in the following example.

EXAMPLE 9

The THF solution of the hydroborated polysilazane (Polymer II) in Example 8 was cannulated into a sparged, 250 ml, one-necked flask containing 80.0 g Starck A-10 α-SiC powder. The mixture was stirred and the THF was removed in vacuo to give a powder containing 80 wt. % SiC and 20 wt. % hydroborated polysilazane (≈0.5 g B content). The mixture was hot-pressed under the following conditions: argon atmosphere, 10°C/min ramp from 25°C to 2100°C. After reaching 2100°C, the sample was maintained at this temperature for 2 hours and then cooled to room temperature. Examination of a fractured surface via SEM shows that the material had sintered and densified. Fully connected grains were present. The fracture was smooth and no grain boundary

phase was observed. The hot-pressed piece had a density of 3.01 g/cc. The X-ray diffraction pattern showed only α-SiC.

EXAMPLE 10

A 500 ml, one-necked, round-bottomed flask was equipped with a stir bar and charged with 80.0 g of Starck A-10 α-SiC. The flask was topped with a septum and then charged with 20.0 g of methylvinylsilazane, $(MeSiViNH)_x$ and 300 ml of hexane by syringe. The mixture was stirred as the hexane was removed in vacuo to give a dry powder. This mixture was hot-pressed under the following conditions: argon atmosphere, 10°C/min ramp from 25°C to 2100°C. After reaching 2100°C, the sample was maintained at this temperature for 2 hours and then cooled to room temperature. The hot-pressed sample had a density of only 2.0 g/cc. By SEM, the piece had semi-connected grains with many pores.

EXAMPLE 11

A 250 ml, three-necked round-bottom flask was sparged with nitrogen and equipped with a 50 ml dropping funnel, a thermometer, a stir bar, and a septum. The flask was charged with 38.38 ml (38.38 mmol) BH_3•THF adduct and cooled to 0°C in an ice bath. The dropping funnel was charged with 7.78 ml (76.7 mmol) cyclohexene and 36 ml tetrahydrofuran (THF). The cyclohexene/THF mixture was added dropwise over 45 min. A white solid (dicyclohexylborane) formed. The reaction mixture was stirred for one hour at 0°C. The dropping funnel was then charged with 13.0 g (202.0 mmol)

poly(methylvinyl)silazane, $[MeSiHNH)_{0.8}$ $(MeSiViNH)_{0.2}]_x$ and 36 ml THF and added to the reaction mixture over 30 min. After the polysilazane addition was complete, the reaction mixture was stirred for 30 min at 0°C and then warmed to room temperature. The white solid disappeared and a clear solution was formed. The boron-substituted polysilazane, Polymer III, contained 2.1 wt. % boron bound to the polymer backbone. This solution was used in the following example.

EXAMPLE 12

The THF solution of the hydroborated polysilazane (Polymer III) in Example 11 was cannulated into a sparged, 500 ml, one-necked flask containing 79.8 g Starck A-10 α-SiC powder. The mixture was stirred and the THF was removed in vacuo to give a powder containing 80 wt. % SiC and 20 wt. % hydroborated polysilazane (≈0.42 g B content). The mixture was hot-pressed under the following conditions: argon atmosphere, 10°C/min ramp from 25°C to 2100°C. After reaching 2100°C, the sample was maintained at this temperature for 2 hours and then cooled to room temperature. Examination of a fractured surface via SEM shows that the material had sintered and densified. Fully connected grains were present. The fracture was smooth and no grain boundary phase was observed. The hot-pressed piece had a density of 3.0 g/cc. The X-ray diffraction pattern showed only α-SiC.

EXAMPLE 13

The hydroborated polysilazane Polymer III solution in THF was prepared as described in Example 11. This solution was cannulated into a sparged, 500 ml, one-necked flask containing 79.8 g Starck B-10 ß-SiC powder. The mixture was stirred and the THF was removed in vacuo to give a powder containing 80 wt. % SiC and 20 wt. % hydroborated polysilazane (≈0.42 g B content). The mixture was hot-pressed under the following conditions: argon atmosphere, 10°C/min ramp from 25°C to 2100°C. After reaching 2100°C, the sample was maintained at this temperature for 2 hours and then cooled to room temperature. Examination of a fractured surface via SEM shows that the material had sintered and densified. Fully connected grains were present. The fracture was smooth and no grain boundary was observed. The hot-pressed piece had a density of 3.1 g/cc. The X-ray diffraction pattern showed only α-SiC.

EXAMPLE 14

In a dry box, a sample (≈0.5 ml) of the liquid boron-substituted polysilazane Polymer I was placed in a small quartz Erlenmeyer flask and closed with a septum. The septum was covered with foil and the flask was exposed to a broad band mercury light at a distance of about six inches. The sample temperature did not rise above 30°C. After exposure for 97 3/4 h, a solid, cured material was produced.

EXAMPLE 15

A sample of boron-substituted polysilazane, i.e., Polymer II, which had a TGA yield of 24.4 wt. %, was prepared and in a dry box transferred to a 2 oz. jar and mixed with 0.5 wt. % dicumyl peroxide. The jar was topped with a septum and removed from the dry box. The jar was placed in a preheated 160°C oil bath with a nitrogen inlet in the septum. After several hours the mixture cured to a rubbery solid. This solid had a TGA yield of 49.2 wt. %. After cooling to room temperature, the jar was taken into the dry box and the sample divided into three parts. Each portion of the cured Polymer II was subjected to pyrolysis at 10°C/min under Ar to 1400°C, 1600°C and 1800°C. After a two hour hold at each maximum temperature, the black samples were cooled to room temperature and X-ray diffraction analysis was conducted. After heating to 1400°C, the sample was substantially amorphous, although broad peaks in the correct region for ß-SiC and small peaks for α-SiC were observed. These peaks became sharper and more distinct in the X-ray pattern for the sample pyrolyzed at 1600°C, although some amorphous material was still present. The X-ray sample pyrolyzed to 1800°C showed intense, sharp peaks for crystalline ß-SiC and small peaks for α-SiC.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A boron-substituted polysilazane composition characterized in that the boron is derived from a borane and is bound to the polysilazane through boron-carbon bonds.

2. The composition of claim 1, further characterized in that the polysilazane contains at least one member selected from the group consisting of alkenyl groups and alkynyl groups.

3. The composition of claim 2, further characterized in that the alkenyl groups are vinyl groups or allyl groups.

4. The composition of claim 2, further characterized in that it additionally comprises a free radical generator.

5. The composition of claim 4, further characterized in that the free radical generator is a peroxide or an azo compound.

6. The composition of claim 5, further characterized in that the peroxide is selected from dicumyl peroxide, t-butyl cumyl peroxide, bis-2,4-dichlorobenzoyl peroxide, t-butyl perbenzoate, t-butyl peracetate, 2,5-di(t-butylperoxy)hexane, and di-t-butylperoxide.

7. The composition of claim 5, further characterized in that the azo compound is selected from 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), 2,2'-azobis(2-methyl-propionitrile), and 2-(t-butylazo)isobutyronitrile.

8. The composition of any of the preceding claims, further characterized in that it additionally comprises a filler.

9. The composition of claim 8, further characterized in that the filler is selected from SiC, Si_3N_4, SiO_2, BN, AlN, Al_2O_3, TiN, TiC, ZrC, Si, Ti, Zr, ZrO_2, B_4C and Y_2O_3.

10. The composition of claim 9, further characterized in that the filler is selected from the group consisting of α-SiC, ß-SiC, and mixtures of α-SiC and ß-SiC.

11. A process for preparing a boron-substituted polysilazane characterized by:

(a) preparing a silazane ammonolysis product by reacting ammonia with a halogenated silicon compound selected from the group consisting of $RSiX_3$, $RR'SiX_2$, $RR'R''SiX$, SiX_4 and mixtures thereof, wherein X is selected from the group consisting of Cl, Br and I; and R, R' and R'' are the same or different and are selected from the group consisting of H, substituted or unsubstituted 1-6 carbon alkyl groups, aryl groups, 2-6 carbon alkenyl groups and 2-6 carbon alkynyl groups, and wherein at least one of the

halogenated silicon compounds comprises at least one member selected from the group consisting of alkenyl groups and alkynyl groups; and

(b) reacting the silazane ammonolysis product with a borane containing at least one B-H group per molecule under conditions and for a time sufficient to form a boron-substituted polysilazane wherein the boron is derived from the borane and is bound to the polysilazane through boron-carbon bonds.

12. The process of claim 11, further characterized in that the halogenated silicon compound is a member selected from the group consisting of $RSiX_3$, and $RR'SiX_2$.

13. The process of claims 11 or 12, further characterized in that the halogenated silicon compounds containing alkenyl groups are selected from the group consisting of methylvinyldichlorosilane, vinyltrichlorosilane, dimethylvinylchlorosilane, phenylvinyldichlorosilane, allylmethyldichlorosilane, allyltrichlorosilane and 4-but-1-enyldichloromethylsilane.

14. The process of claims 11-13, further characterized in that the borane is selected from the group consisting of $RR'BH$, RBH_2, and $BH_3 \bullet L$, in which R and R' are the same or different and are selected from the group consisting of 1-10 carbon alkyl groups, aryl groups, 2-6 carbon alkenyl groups, and 2-6 carbon alkynyl groups, and L is a Lewis base donor.

15. The process of claim 14, further characterized in that the borane is dicyclohexylborane.

16. Use of the compositions of claims 2-7 to prepare a crosslinked boron-substituted polysilazane characterized by supplying energy to generate free radicals.

17. The use of claim 16 characterized by supplying energy in the form of heat, UV irradiation, electron beam irradiation, or gamma ray irradiation.

18. Use of the composition of claims 1-10 to prepare an amorphous boron-containing char consisting essentially of boron, carbon, silicon, and nitrogen wherein the boron is homogeneously distributed throughout the char and is essentially devoid of elemental boron and boron carbide.

19. Use of the composition of claims 1-10 to prepare a silicon carbide-containing ceramic article.