AUSTRALIA

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the persons identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: DOW CORNING CORPORATION

Address: P.O. BOX 994, MIDLAND, MICHIGAN 48686-0994, UNITED STATES OF AMERICA

[70] Nominated Person: DOW CORNING CORPORATION

Address: P.O. BOX 994, MIDLAND, MICHIGAN 48686-0994, UNITED STATES OF AMERICA

[54] Invention Title: PREPARATION OF HIGH DENSITY TITANIUM DIBORIDE CERAMICS WITH PRECERAMIC POLYMER BINDERS

[72] Name(s) of actual inventor(s): GREGG ALAN ZANK

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
281,812	UNITED STATES OF AMERICA	US	28 JULY 1994

Basic Applicant(s): GREGG ALAN ZANK

Drawing number recommended to accompany the abstract .....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....

DATED this 26th day of July 1995.

Ian A. Scott

Registered Patent Attorney

M071060 260795

690699

AUSTRALIA

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

Patents Act 1990

NOTICE OF ENTITLEMENT

We, **DOW CORNING CORPORATION** of P. O. Box 994, Midland, Michigan 48686-0994, United States of America, being the applicant in respect of Application No. **27207/95** state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventor by assignment.

The person nominated for the grant of the patent has entitlement from the applicant of the basic application listed on the patent request form by assignment.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

DOW CORNING CORPORATION
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....

9 February 1998

Ian A. Scott
Registered Patent Attorney

AU9527207

(12) PATENT ABRIDGMENT (11) Document No. AU-B-27207/95
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 690699

(54) Title
PREPARATION OF HIGH DENSITY TITANIUM DIBORIDE CERAMICS WITH PRECERAMIC POLYMER BINDERS

International Patent Classification(s)
(51)[6] C04B 035/58

(21) Application No. : 27207/95 (22) Application Date : 26.07.95

(30) Priority Data

(31) Number	(32) Date	(33) Country
281812	28.07.94	US UNITED STATES OF AMERICA

(43) Publication Date : 08.02.96

(44) Publication Date of Accepted Application : 30.04.98

(71) Applicant(s)
DOW CORNING CORPORATION

(72) Inventor(s)
GREGG ALAN ZANK

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
US 4336215
GB 2015498
GB 2002738

The present invention provides a method for preparing a sintered titanium diboride ceramic body. The method comprises blending titanium diboride powder and at least 10% by weight preceramic organosilicon polymer to a uniform mixture. The preceramic organosilicon polymer is one which provides at least a stoichiometric amount of carbon based on the silicon content. The uniform mixture is then formed into the desired shape to obtain a handleable green body. The handleable green body is then sintered in an inert atmosphere at a temperature greater than 2000°C. to obtain a sintered body with a density greater than 90% of the theoretical density for titanium diboride.

The present invention introduces the preparation of high density sintered titanium diboride bodies from preceramic organosilicon polymers and titanium diboride powder. These sintered bodies are produced by this invention and have densities greater than 90% of the theoretical density of titanium diboride. Such highly densified bodies are useful, for example, in wear parts and the nuclear industry.

.../2

Claim

1. A method of forming a handleable green body comprising:

(a) mixing components comprising titanium diboride powder and at least 10% by weight preceramic organosilicon polymer to a uniform mixture, wherein the preceramic organosilicon polymer is one which provides at least a stoichiometric amount of carbon based on the silicon content; and

(b) forming the uniform mixture into a desired shape to obtain said handleable green body.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: PREPARATION OF HIGH DENSITY TITANIUM DIBORIDE CERAMICS WITH PRECERAMIC POLYMER BINDERS

The following statement is a full description of this invention, including the best method of performing it known to us :-

PREPARATION OF HIGH DENSITY TITANIUM DIBORIDE CERAMICS WITH PRECERAMIC POLYMER BINDERS

This invention relates to the preparation of high density titanium diboride ceramic bodies by the pyrolysis of mixtures comprising titanium diboride powder and preceramic organosilicon polymers.

Titanium diboride ceramic bodies are known in the art. They have found particular utility, for example, as wear parts and in the nuclear industry because of their high hardness, resistance to wear and nuclear properties. Early methods for producing these bodies involved hot-pressing titanium diboride powder at temperatures up to 2300°C. This method, however, has a number of disadvantages. First, the method does not produce green bodies and, as such, does not allow for green machining. Second, the process is expensive because it requires the use of high pressure during sintering. Finally, it is difficult to form bodies of complex size and shape by hot pressing methods.

An alternative approach to producing titanium diboride bodies is to use fugitive binders to form green titanium diboride bodies and to then pressureless sinter these green bodies. In this approach, however, the binder must be pyrolyzed out of the bodies. As such, the process takes additional time and the ceramic bodies undergo significant shrinkage which may result in warpage or cracks.

U.S. Patent 4,289,720 teaches a process for the formation of ceramic fired bodies. The process comprises molding mixtures of organosilicon polymers and ceramic powders to form green bodies followed by pyrolyzing the green bodies to form ceramic bodies. However, over 150 ceramic powders (including titanium diboride) are listed

therein whereas the examples only show densification of silicon carbide, silicon nitride and boron carbide. Moreover, the patent only utilizes temperatures up to 2000°C. (temperatures in the range of 1550-1800°C. are preferred) (col. 9, lines 1-4). We have found that such temperatures are not sufficient to satisfactorily complete the polymer pyrolysis. As such, the density of our bodies are superior.

Japanese Kokai Publication 4-300251 shows a process for producing titanium boride sintered bodies. The method comprises mixing a silicone resin, a sintering assistant and titanium boride powder, molding the mixture and then sintering. This publication, however, requires the addition of a sintering assistant to form dense bodies. Moreover, the reference teaches the use of 10 parts or less of silicone resin to 100 parts of titanium boride powder (9% by weight silicone).

The object of the present invention is to provide a method for producing high density and high strength bodies of titanium diboride ceramic. Such ceramics can unexpectedly be obtained by sintering a mixture comprising a preceramic organosilicon polymer and titanium diboride powder.

The present invention provides a method for preparing a sintered titanium diboride ceramic body. The method comprises blending titanium diboride powder and at least 10% by weight preceramic organosilicon polymer to a uniform mixture. The preceramic organosilicon polymer is one which provides at least a stoichiometric amount of carbon based on the silicon content. The uniform mixture is then formed into the desired shape to obtain a handleable green body. The handleable green body is then sintered in

an inert atmosphere at a temperature greater than 2000°C. to obtain a sintered body with a density greater than 90% of the theoretical density for titanium diboride.

The present invention introduces the preparation of high density sintered titanium diboride bodies from preceramic organosilicon polymers and titanium diboride powder. These sintered bodies are produced by this invention and have densities greater than 90% of the theoretical density of titanium diboride. Such highly densified bodies are useful, for example, in wear parts and the nuclear industry.

As used herein, the theoretical density of titanium diboride is 4.52 g/cm^3. As discussed infra, however, the ceramic bodies of this invention generally contain some SiC and B_4C in the intergranular pores. The theoretical amount of SiC and B_4C in a ceramic body is taken into consideration when calculating densities.

The first step of our invention comprises blending the organosilicon polymer with the titanium diboride powder. The organosilicon polymers useful in this invention are generally well known in the art. Organosilicon polymers with a significant ceramic char yield are preferred because the amount of binder shrinkage that occurs upon pyrolysis decreases as the char yield increases. Preferably, therefore, the ceramic char yield is greater than 20 weight percent. More preferably, organosilicon polymers with ceramic char yields greater than 35 weight percent are employed. Most preferably, organosilicon polymers with ceramic char yields greater than 45 weight percent are employed.

The organosilicon polymer must also yield a ceramic char containing at least enough carbon to form

silicon carbide with the silicon present in the char (hereafter a "stoichiometric amount"). Excess carbon in the char is often preferred because it assists in removing oxygen and thus, the densification of the ceramic body. This excess carbon is referred to as "free carbon" (i.e., excess carbon present in the char over the amount of carbon needed to form silicon carbide with the silicon present in the char). It is often preferred that the ceramic char contain at least 10 weight percent free carbon. It is often more preferred that the ceramic char contain at least 25 weight percent free carbon.

Organosilicon polymers within the scope of this invention include polysiloxanes, polysilazanes, polysilanes and polycarbosilanes. If the organosilicon polymer is an organopolysiloxane, it may contain units of general structure $[R_3SiO_{0.5}]$, $[R_2SiO]$, $[RSiO_{1.5}]$ and $[SiO_2]$ where each R is independently selected from hydrogen atom, alkyl radicals containing 1 to 20 carbon atoms such as methyl, ethyl and propyl; aryl radicals such as phenyl and unsaturated hydrocarbon radicals such as vinyl. Examples of specific organopolysiloxane groups include $[PhSiO_{1.5}]$, $[MeSiO_{1.5}]$, [MePhSiO], $[Ph_2SiO]$, [PhViSiO] $[ViSiO_{1.5}]$, [MeHSiO], [MeViSiO], $[Me_2SiO]$, $[Me_3SiO_{0.5}]$ and the like. Mixtures of organopolysiloxanes may also be employed. As used throughout this specification, Me represents methyl, Vi represents vinyl and Ph represents phenyl.

The organopolysiloxanes of this invention are prepared by techniques well known in the art. The actual method used to prepare the organopolysiloxane is not critical. Most commonly, the organopolysiloxanes are prepared by the hydrolysis of organochlorosilanes. Such

methods, as well as others, are described in Noll, Chemistry and Technology of Silicones, Chapter 5 (translated 2d Ger. Ed., Academic Press, 1968).

The organopolysiloxane may also be substituted with various metallo groups (i.e., containing repeating metal-O-Si units). Examples of suitable compounds include borosiloxanes and alumosiloxanes which are both well known in the art. For instance, Noll, Chemistry and Technology of Silicones, Chapter 7, (translated 2d Ger. Ed., Academic Press, 1968) discloses numerous polymers of this type as well as their method of manufacture. Additionally, Japanese Kokai Publication 54-134744; U.S. Patent 4,455,414 and U.S. Patent 5,112,779 also discuss the preparation and utility of various polymetallosiloxanes as binders for SiC powder which have utility in our invention.

If the preceramic organosilicon polymer is a polysilazane, it may contain units of the type $[R_2SiNH]$, $[RSi(NH)_{1.5}]$ and/or $[R'_2CR''_2CR'''_2CSiNH]$ where each R is independently selected from hydrogen atom, alkyl radicals containing 1 to 20 carbon atoms such as methyl, ethyl and propyl; aryl radicals such as phenyl and unsaturated hydrocarbon radicals such as vinyl and each R', R'' and R''' is independently selected from hydrogen atom, alkyl radicals having 1 to 4 carbon atoms, aryl radicals such as phenyl and unsaturated hydrocarbon radicals such as vinyl. Examples of specific polysilazane units include $[Ph_2SiNH]$, $[PhSi(NH)_{1.5}]$, $[CH_2CH_2CH_2SiNH]$, $[MeSi(NH)_{1.5}]$, $[Me_2SiNH]$,

[$ViSi(NH)_{1.5}$], [Vi_2SiNH], [PhMeSiNH], [$HSi(NH)_{1.5}$], [PhViSiNH] and [MeViSiNH].

The polysilazanes of this invention can be prepared by techniques well known in the art. The actual method used to prepare the polysilazane is not critical. Suitable preceramic silazane polymers or polysilazanes may be prepared by the methods of U.S. Patents 4,312,970; 4,340,619; 4,395,460 and 4,404,153. Suitable polysilazanes also include those prepared by the methods of U.S. Patents 4,482,689 and 4,397,828. Other polysilazanes suitable for use in this invention can be prepared by U.S. Patents 4,540,803 and 4,543,344; or by Burns et al. in J. Mater. Sci, 22 (1987), pp 2609-2614 and similarly in U.S. Patents 4,835,238; 4,774,312; 4,929,742 and 4,916,200.

The polysilazane may also be substituted with various metal groups (i.e., containing repeating metal-N-Si units). Examples of suitable compounds include borosilazanes which are known in the art. These include those described in U.S. Patents 4,910,173; 4,482,689; 5,164,344; 5,252,684; 5,169,908 and 5,030,744. It also includes borosilazanes described by Seyferth et al., J. Am. Ceram. Soc. 73, 2131-2133 (1990); Noth, B. Anorg. Chem. Org. Chem., 16(9), 618-21, (1961); and EP-A 0,364,323.

If the preceramic organosilicon polymer is a polysilane, it may contain units of general structure [R_3Si], [R_2Si] and [RSi] where each R is independently selected from hydrogen atom; alkyl radicals containing 1 to 20 carbon atoms such as methyl, ethyl and propyl; aryl radicals such as phenyl and unsaturated hydrocarbon radicals such as vinyl. Examples of specific polysilane units are [Me_2Si], [PhMeSi], [MeSi], [PhSi], [ViSi], [PhMeSi], [MeHSi], [MeViSi], [Ph_2Si], [Me_2Si] and [Me_3Si].

The polysilanes of this invention can be prepared by techniques well known in the art. The actual method used to prepare the polysilanes is not critical. Suitable polysilanes may be prepared by the reaction of organohalosilanes with alkali metals as described in Noll, Chemistry and Technology of Silicones, 347-49 (translated 2d Ger. Ed., Academic Press, 1968). More specifically, suitable polysilanes may be prepared by the sodium metal reduction of organo-substituted chlorosilanes as described in U.S. Patent 4,260,780 and 25 Polym. Preprints 4 (1984). Other suitable polysilanes can be prepared by the general procedures described in U.S. Patent 4,298,559.

The polysilane may also be substituted with various metal groups (i.e., containing repeating metal-Si units). Examples of suitable metals to be included therein include boron, aluminum, chromium and titanium. The method used to prepare said polymetallosilanes is not critical. It may be, for example, the method of U.S. Patent 4,762,895 or 4,906,710.

If the preceramic organosilicon polymer is a polycarbosilane, it may contain units of the type $[R_2SiC]$, $[RSiC_{1.5}]$ and/or $[R_3SiC]$ where each R is independently selected from hydrogen atom; alkyl radicals containing 1 to 20 carbon atoms such as methyl, ethyl and propyl; aryl radicals such as phenyl and unsaturated hydrocarbon radicals such as vinyl. Suitable polymers are described, for instance, in U.S. Patents 4,052,430 and 4,100,233. Polycarbosilanes containing repeating $(-SiHCH_3-CH_2-)$ units can be purchased commercially from the Nippon Carbon Co.

The polycarbosilane may also be substituted with various metal groups such as boron, aluminum, chromium and titanium. The method used to prepare such polymers is not

critical. It may be, for example, the methods of U.S. Patents 4,248,814, 4,283,376 and 4,220,600.

The above organosilicon polymers which contain vinyl groups may be preferred since vinyl groups attached to silicon provide a mechanism whereby the organosilicon polymer can be cured prior to sintering. Also, mixtures of any of the above organosilicon compounds are also contemplated by this invention.

Specific methods for preparation of suitable organosilicon polymers are illustrated in the following examples.

The use of organosilicon polymers as binders for titanium diboride powder is particularly advantageous over binders of the prior art since a polymer can be chosen which will provide a suitable char yield and, if desired, additional free carbon. In this manner, the polymer can be tailored to obtain a polymer/titanium diboride ratio in the preceramic mixture which is suitable for any molding application to be utilized.

The preceramic organosilicon polymer is present in the compositions of the present invention in an amount of at least 10% by weight. Generally, the content of the polymer is less than 50 wt% and often it is less than 30 wt%. The exact amount of polymer, however, is dependent on the method of molding used. For instance, for standard cold-isostatic pressing the preferred amount of polymer is in the range of 10-20 wt%. For extrusion, the preferred amount of polymer is in the range of 15-25 wt%.

The compositions of the invention also include titanium diboride powders. These powders are commercially available and are well known in the art, for instance, from Starck™. Generally, titanium diboride powders with a

number average particle size of less than 10 μm are preferred; powders with a number average particle size of less than 5 μm are more preferred; and those with a number average particle size less than 1 μm are most preferred.

The compositions of this invention may also contain curing agents which are used to cause the organosilicon polymer to crosslink prior to sintering. The green bodies produced thereby generally have higher strengths than the uncured articles. Thus, they can better withstand any handling or machining processes prior to sintering. These curing agents are generally activated by heating the green body containing the curing agent to temperatures in the range of 50-500°C.

Conventional curing agents which are useful in the present invention are well known in the art. Examples include organic peroxides such as dibenzoyl peroxide, bis-p-chlorobenzol peroxide, bis-2,4-dichlorobenzol peroxide, di-t-butyl peroxide, dicumyl peroxide, t-butyl perbenzoate, 2,5-bis(t-butylperoxy)-2,3-dimethylhexane and t-butyl peracetate; and platinum-containing curing agents such as platinum metal, H_2PtCl_6 and $((C_4H_9)_3P)_2PtCl_2$. Other conventional curing agents known in the art may also be used. The curing agent is present in an effective amount, i.e., an amount sufficient to induce crosslinking in the polymer. Therefore, the actual amount of the curing agent will depend on the activity of the actual agent used and the amount of polymer present. Normally, however, the peroxide curing agent will be present at 0.1 to 5.0 weight percent based on the weight of the compound to be cured with the preferred amount being 2.0 weight percent. When platinum-containing curing agents are used, the amount will normally be such that platinum is present at 1 to 1000 ppm based on

the weight of the compound to be cured with the preferred amount being 50 to 150 ppm platinum.

In addition to the above curing agent, a crosslinking agent may also be included in the mixture to crosslink the polymer and, thereby, to modify the cure characteristics. These agents can include, for example, polyfunctional silanes or siloxanes. The preferred crosslinking agents are siloxanes with Si-H functional bonds such as $Ph_2Si(OSiMe_2H)_2$ or $PhSi(OSiMe_2H)_3$.

The addition of other processing aids such as lubricants, deflocculants and dispersants is also permissible in this invention. Examples of such compounds include stearic acid, mineral oil, paraffin, calcium stearate, aluminum stearate, succinic acid, succinimide, succinic anhydride or various commercial products such as Oloa 1200™.

Once the amounts of the various components have been determined, they are combined in a manner which assures a uniform and intimate mixture so that areas of varying density throughout the sintered product are avoided. Uniform and intimate mixtures can be prepared by using conventional blending techniques such as grinding the various powders in either the dry or wet state or the use of ultrasonic dispersion. Other mixing and grinding methods will be apparent to those skilled in the art.

The above mixture is then formed into a handleable green body. "Handleable green body" means green bodies which have sufficient green strength to be handled or machined to a desired shape prior to sintering. Generally, green strengths of 20 kg/cm^2 or more may be obtained in the practice of this invention. This green strength is achieved primarily because the preceramic mixture includes an

organosilicon polymer which acts as a matrix for the titanium diboride powder. The increased green strength obtained by the practice of this invention alleviates the problems associated with handling fragile objects and allows for the production of more complex shapes through machining or milling.

The handleable green bodies may be formed by conventional techniques known in the art. Such methods include hot pressing, dry pressing, slip casting, pressure molding, uniaxial pressing, isopressing, extrusion, transfer molding and injection molding. The present invention is particularly advantageous in this respect since the amount of polymer in the preceramic mixture can easily be changed to accommodate the use of multiple molding techniques without affecting the quality of the sintered product.

The composition is preferably cured prior to its final shaping. Curing procedures are well known in the art. Generally, such curing can be carried out by heating the article to a temperature in the range of 50 to 500°C., preferably in an inert atmosphere such as argon or nitrogen.

The shaped green bodies are then fired to an elevated temperature under an inert atmosphere to convert them into ceramic articles having densities greater than about 90% of theoretical. Upon pyrolysis, the organosilicon polymers of this invention yield SiC and, optionally, free carbon. Additionally, the interaction of the polymer and the titanium diboride powder generally yields boron carbide. These factors tend to decrease the amount of shrinkage that occurs when the mixture is sintered since the SiC and B_4C forms in the intergranular pores of the titanium diboride powder, thus limiting the shrinkage due to densification.

Because less shrinkage occurs, sintered objects with increased tolerance control can surprisingly be formed.

The compositions of this invention may be sintered either under pressure or by using a pressureless process to produce a highly densified ceramic article. Since the sintering process employing pressure will generally produce ceramic articles with higher density, such a method would be preferred if maximum density were desired. Generally, however, the pressureless sintering process is preferred because of the simplified operations involved.

Inert atmospheres are used for sintering to prevent oxygen incorporation and silica formation. The sintering process as well as the density of the sintered product are thereby enhanced. For this invention, an "inert atmosphere" includes an inert gas, vacuum or both. If an inert gas is used, it may be argon, helium or nitrogen. If a vacuum is used, it may be in the range of 13.3 - 26,664.0 Pa (0.1-200 torr), preferably 13.3 - 40.0 Pa (0.1-0.3 torr). Exemplary of a combined process might be firing the composition in argon up to 1200°C., firing from 1200 to 1500°C. in a vacuum and firing from 1500 to 2150°C. under argon.

Sintering may be performed in any conventional high temperature furnace equipped with a means to control the furnace atmosphere. Temperatures of greater than 2000°C. are generally used with the preferred range being 2100-2250°C. The most preferred sintering temperature is about 2150°C. Though lower temperatures can be used, the ceramic product may not possess the desired density.

The temperature schedule for sintering depends on both the volume of parts to be fired and the composition of the mixture. For smaller objects, the temperature may be

elevated rapidly. For larger objects, or those with large concentrations of the organosilicon polymer, however, more extended programs are needed to create uniform ceramic bodies.

The resultant ceramic articles have densities greater than 4.00 g/cm^3 of theoretical. It is preferred that the density of the ceramic article be greater than 4.3 g/cm^3 of theoretical. Our ceramic bodies generally have strengths greater than 15 kg/m^2 and often in excess of 30kg/m^2. Such bodies comprise a mixture of mainly titanium diboride with a small amount of boron carbide and silicon carbide being present (e.g., less than 10% of the total ceramic weight). Generally, the bodies contain 2-10 wt% (e.g., 2-8 wt%) silicon carbide, up to 3 wt% (e.g., 0.1-3 wt%) boron carbide, up to 2 wt% (e.g., 0.1-2 wt%) free carbon and 87-98 wt% titanium diboride. The expression "titanium diboride body" is used herein to describe these ceramic bodies.

So that those skilled in the art can better appreciate and understand the invention, the following examples are presented. Unless otherwise indicated, all percentages are by weight.

In the following examples, the analytical methods used were as follows:

Proton NMR spectra were recorded on either a Varian™ EM360 or FT200 spectrometer and the results presented herein are in ppm. Fournier transform IR spectra were recorded on a Perkin Elmer™ 7700 FT spectrometer. Gel permeation chromatography (GPC) data were obtained on a Waters™ GPC equipped with a model 600E systems controller, a model 490 UV and model 410 Differential Defractometer detectors; all values are relative to polystyrene. TGA and

TMA data were recorded on a Du Pont™ 940 thermomechanical analyzer (TMA) and an Omnitherm™ thermal gravimetric analyzer (TGA) interfaced to an IBM™ 386 Computer.

Carbon, hydrogen and nitrogen analysis were done on a Control Equipment Corporation™ 240-XA Elemental Analyzer. Oxygen analysis was done on a Leco™ Oxygen Analyzer equipped with an Oxygen Determinator 316 (Model 783700) and an Electrode Furnace EF100. Silicon was determined by a fusion technique which consisted of converting the material to soluble forms of silicon and analyzing the solute for total silicon by atomic absorption spectrometry.

Compounding was done with a Hauschild™ Dental Mixer. A 10.9 Mg (12 ton) Hull™ console molding machine (model 359E) was used for transfer molding.

Fired densities were measured by water immersion techniques according to ASTM C373-72.

Example 1

Hot Press sintering of titanium diboride powder using a siloxane binder

A. Polymer Synthesis

A mixture of 476 g of $PhSi(OMe)_3$, 286 g of $MeSi(OMe)_3$ and 137.5 g $(ViMe_2Si)_2O$ was added to a solution of 4 g of trifluoromethane sulfonic acid in 400 g of water. After approximately 20 minutes, the solution was refluxed for 12 hours. The solution was cooled and then neutralized with 3.5 g of potassium carbonate. The volatiles were removed by distillation until an internal temperature of 110°C. was reached. The reaction mixture was cooled and 700 g of toluene and 70 g of a 3 wt% solution of KOH in water were added. The solution was refluxed and the water removed in a Dean-Stark trap. After water removal, the mixture was

cooled and 27 mL of $Me_2ViSiCl$ were added. After stirring at room temperature for 2 hours, the mixture was filtered through a 0.2 μm membrane filter and the filtrate concentrated by rotary evaporation. The residue was dried for 1-2 hours at 100°C. and less than 133.3 Pa (1 torr). The yield was 553.3 g.

B. Polymer Pyrolysis and Char Composition Calculations

A blend of 6.554 g of the resin formed in part A and 0.06 g Lupersol™ (bis (t-butyl peroxy-2,5-dimethyl-hexane) was prepared. An aliquot of the blend was crosslinked at 180°C. for one hour. An aliquot of the crosslinked polymer was weighed into a graphite crucible. The crucible was transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C./minute and held at temperature for 1 hour before cooling to room temperature. The sample had a mass retention of 41.8%. The elemental composition of the char was 38.1% carbon and 61.6% silicon (by difference). The following calculation was made: 100 g of cured polymer gives 41.8 g of a ceramic char consisting of 25.9 g silicon and 15.9 g carbon. The char consists of 36.97 g of SiC (88.43%) and 4.83 g C (11.57%). Therefore, every g of polymer gives 0.369 g of SiC and 0.048 g of excess C.

C. Mix Preparation and Hot pressing

A mix was prepared using the following procedure: 14 g of the resin prepared in part A, 200 mL of toluene and 0.50 g Lupersol™ were mixed with 84 g of Starck™ Grade A titanium diboride powder in a beaker. The mixture was ultrasonicated for 5 minutes and transferred to a round

bottom flask. The solvent was removed in vacuo and the residue further dried. The dried powder was ground in a mortar and pestle and then sieved through a 90 μm mesh sieve. An aliquot of the above mixture was fired to 2100°C. in argon using the following program: room temperature to 2100°C. at 15°C./minute with a 1 hour hold at temperature. A pressure of 27.6 MPa (4 ksi) was applied to the sample during the firing cycle. The density of the resultant piece was 4.35 g/cm^3. ASTM 4 point bend bars of nominal dimensions of 2 x 1.5 x 20 mm were machined from the sample and were found to have bend strengths of 4192.3 ± 437.5 kg/mm^2.

Examples 2-5

Pressureless sintering of titanium diboride powder using siloxane binder

Ex 2. Test Bar Fabrication and Firing

An aliquot of the mix prepared in Example 1C was dry pressed into test bars 35 x 8 x 2 mm in a WC lined die with a Carver™ laboratory press at 3220 kg/cm^2. The test bars were heated to 250°C. for 24 hours to crosslink the polymer. The test bars were fired to 2100 or 2150°C. in argon using the following program: room temperature to 1200°C. at 5°C./minute, a 30 minute hold, 1200-1400°C. at 5°C./minute under vacuum and 1400°C. to final temp at 5°C./minute with a 60 minute hold at temperature. The test bars are characterized in Table 1.

Ex 3. Test Bar Fabrication and Firing

A mixture was prepared by mixing 5.73 g of the resin in Example 1, 0.05 g Lupersol™, 200 mL of toluene and 40.9 g of Starck™ Grade A titanium diboride powder. The mixture was ultrasonicated for 5 minutes and transferred to a round bottom flask. The solvent was removed in vacuo and

the residue further dried. The dried powder was ground in a mortar and pestle and then sieved through a 90 μm mesh sieve. The sieved powder was pressed, crosslinked and fired as in Example 2. The test bars are characterized in Table 1.

Ex 4. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in Example 1, 0.2 g Lupersol™, 200 mL of toluene and 87 g of Starck™ Grade A titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Ex 5. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in Example 1, 0.2 g Lupersol™, 200 mL of toluene and 87 g of Starck™ Grade F titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Examples 6-7

Pressureless sintering of titanium diboride powder using siloxane binder

A. Polymer Synthesis

A mixture of 3960 g of $PhSi(OMe)_3$ and 620 g $(ViMe_2Si)_2O$ was added to a solution of 3 g of trifluoromethane sulfonic acid in 800 g of water. After approximately 20 minutes, the solution was refluxed for 5 hours. The solution was cooled and then neutralized with

2.73 g of potassium carbonate. The volatiles were removed by distillation until an internal temperature of 120°C. was reached. The reaction mixture was cooled and 1500 g of toluene and 125.7 g of a 3 wt% solution of KOH in water were added. The solution was refluxed and the water removed in a Dean-Stark trap. After water removal, the mixture was cooled and 20 mL of $Me_2ViSiCl$ were added. After stirring at room temperature for 2 hours, the mixture was filtered through a 0.2 μm membrane filter and the filtrate concentrated by rotary evaporation. The residue was dried for 1-2 hours at 100°C. and less than 133.3 Pa (1 torr). The yield was 3053.3 g.

B. Polymer Pyrolysis and Char Composition Calculations

A blend of 14.85 g of the resin formed in part A, 5.15 g of $Ph_2Si(OSiMe_2H)_2$ and 0.01 g Lupersol™ was prepared. An aliquot of the blend was crosslinked at 120°C. for one hour. An aliquot of the crosslinked polymer was weighed into a graphite crucible. The crucible was transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C./minute and held at temperature for 1 hour before cooling to room temperature. The sample had a mass retention of 44.9%. The elemental composition of the char was 53.4% carbon. The following calculation was made: 100 g of cured polymer gives 44.9 g of a ceramic char consisting of 20.9 g silicon and 24 g carbon. The char consists of 29.9 g of SiC (66.6%) and 15 g C (33.4%). Therefore, every g of polymer gives 0.299 g of SiC and 0.15 g of excess C.

Ex 6. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in section A, 0.2 g Lupersol™, 200 mL of toluene and 87 g of Starck™ Grade A titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Ex 7. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in Example 1, 0.2 g Lupersol™, 200 mL of toluene and 87 g of Starck™ Grade F titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. A test bar was also fired at 1900°C. for comparative purposes. The test bars are characterized in Table 1.

Examples 8-9

Pressureless sintering of titanium diboride powder using polysilane binder

A. Polymer Pyrolysis and Char Composition Calculations

An aliquot of commercially available PSS-400 obtained from Shinn Nisso Kaka Co., Ltd. was weighed into a graphite crucible. The crucible was transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C/minute and held at temperature for 1 hour before cooling to room temperature.

The sample had a mass retention of 44.2%. The elemental composition of the char was 42.3% carbon and 57.7% silicon. The following calculation was made: 100 g of cured polymer gives 44.2 g of a ceramic char consisting of 25.5 g silicon and 18.7 g carbon. The char consists of 34.6 g of SiC (78.3%) and 9.58 g C (21.7%). Therefore, every g of polymer gives 0.346 g of SiC and 0.095 g of excess C.

Ex 8. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in section A, 200 mL of toluene and 87 g of Starck™ Grade A titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Ex 9. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in Example 1, 200 mL of toluene and 87 g of Starck™ Grade F titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were also pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Examples 10-11

Transfer molding of titanium diboride with siloxane binders

A. Cross-linker Synthesis

A high molecular weight SiH functional cross-linker was prepared by mixing 683 g of $Ph_2Si(OMe)_2$, 630 g of $(MeHSiO)_n$ fluid and 61 g of $(Me_3Si)_2O$ in a solution of 2.25

g of trifluoromethane sulfonic acid in 190 g of water and 2 kg of toluene. After approximately 20 minutes, the solution was refluxed for 2 hours. The solution was cooled and then neutralized with 2.73 g of potassium carbonate. Approximately 900 g of volatiles were removed by distillation until an internal temperature of 110°C. was reached. The remaining volatiles were removed by azeotroping to a pot temperature of 120°C. The solution was filtered and rotovaped to yield 1100 g of a siloxane fluid.

B. Polymer Pyrolysis and Char Composition Calculations

A mixture was prepared by mixing 10 g of the resin prepared in Example 1, 1.85 g of the fluid prepared in A and 0.15 g of Lupersol™. An aliquot of the mixture was cross-linked at 180°C. for 1 hour. An aliquot of the cross-linked polymer was weighed into a graphite crucible. The crucible was transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C./minute and held at temperature for 1 hour before cooling to room temperature. The sample had a mass retention of 43.8%. The elemental composition of the char was 37.5% carbon. The following calculation was made: 100 g of cured polymer gives 43.8 g of a ceramic char consisting of 27.4 g silicon and 16.4 g carbon. The char consists of 36.97 g of SiC (89.29%) and 4.83 g C (10.71%). Therefore, every g of polymer gives 0.373 g of SiC and 0.045 g of excess C.

Ex 10. Test Bar Fabrication and Firing

In a 60 mL bowl of a Hauschild™ Dental Mixer was placed 180 g Starck™ Grade A titanium diboride powder, 38.5 g of the resin of Example 1 and 6.5 g of the fluid of A. The mixer was run 4 times at 10 seconds each at which time the mixing was stopped and the material allowed to cool for 5 minutes. 0.5 g Lupersol™ was then added and the mixing continued for 2 times at 6 seconds each and the material removed. This mix was transfer molded into a 12 cavity test bar mold (each cavity = 6.2 x 37.8 x 2.5 mm) at 195°C. with a ram pressure of 87.5 kg/cm^2 and a clamping pressure of 129.5 kg/cm^2. The test bars were fired to 2100 or 2150°C. in argon using the following program: room temperature to 1200°C. at 2.55°C./minute, a 19 minute hold, 1200-1400°C. at 2.5°C./minute under vacuum and 1400°C. to final temp at 2.5°C./minute with a 60 minute hold at temperature. The test bars are characterized in Table 1.

Ex 11. Test Bar Fabrication and Firing

In a 60 mL bowl of a Hauschild™ Dental Mixer was placed 87.5 g Starck™ Grade F titanium diboride powder, 19.25 g of the resin of Example 1 and 3.25 g of the fluid of A. The materials were mixed, pressed and fired in the same manner as Example 10. The test bars are characterized in Table 1.

Examples 12-13

Pressureless sintering of titanium diboride powder using polycarbosilane binder

A. Polymer Pyrolysis and Char Composition Calculations

An aliquot of commercially available polycarbosilane obtained from Nippon Carbon Co., Ltd. was weighed into a graphite crucible. The crucible was

transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C./minute and held at temperature for 1 hour before cooling to room temperature. The sample had a mass retention of 55.8%. The elemental composition of the char was 36.7% carbon and 63.3% silicon. The following calculation was made: 100 g of cured polymer gives 55.8 g of a ceramic char consisting of 63.3 wt% silicon and 37.2 wt% carbon. The char consists of 49.9 g of SiC (84%) and 9.5 g C (16%). Therefore, every g of polymer gives 0.499 g of SiC and 0.090 g of excess C.

Ex 12. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in section A, 200 mL of toluene and 87 g of Starck^{TM} Grade A titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Ex 13. Test Bar Fabrication and Firing

A mixture was prepared by mixing 13 g of the resin in section A, 200 mL of toluene and 87 g of Starck^{TM} Grade F titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2. The test bars are characterized in Table 1.

Examples 14-15

Pressureless sintering of titanium diboride powder using polysilazane binder

A. Polymer Synthesis

A mixture of 610 g of 1,1-dichloro-1-silacyclobutane, 278 g of diphenyldichlorosilane and 375 g of methyltrichlorosilane were dissolved in 8 L of dry toluene and cooled to -78°C. Ammonia was rapidly bubbled through the solution for 3 hours. The reaction temperature was allowed to warm to room temperature and the excess ammonia was distilled off. The reaction was filtered through a medium glass frit and the filtrate concentrated in vacuo. The residue was stripped for 3 hours at 150-175°C. at 133.3 Pa (1 torr).

B. Polymer Pyrolysis and Char Composition Calculations

An aliquot of the above polymer was weighed into a graphite crucible. The crucible was transferred into an Astro tube furnace. The furnace was evacuated to less than 2.67 kPa (20 torr) and then backfilled with argon. This procedure was repeated twice. Under a purge of argon, the sample was heated to 1800°C. at 10°C./minute and held at temperature for 2 hours before cooling to room temperature. The sample had a mass retention of 45.0%. The elemental composition of the char was 50.6% carbon, 48.6% silicon and 0.23% oxygen. The following calculation was made: 100 g of cured polymer gives 45 g of a ceramic char consisting of 48.6 wt% silicon and 50.6 wt% carbon. The char consists of 31.21 g of SiC (70%) and 13.42 g C (30%). Therefore, every g of polymer gives 0.312 g of SiC and 0.134 g of excess C.

Ex 14. Test Bar Fabrication and Firing

A mixture was prepared by mixing 6 g of the resin in section A dissolved in 100 mL of toluene and 44 g of Starck™ Grade A titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3.

The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Ex 15. Test Bar Fabrication and Firing

A mixture was prepared by mixing 6 g of the resin in section A dissolved in 100 mL of toluene and 44 g of Starck™ Grade F titanium diboride powder. The mixture was ultrasonicated, dried, ground and sieved as in Example 3. The sieved powder was pressed, crosslinked and fired as in Example 2, except that 5.1 x 1.3 x 0.6 cm test bars were pressed and fired at 2150 and 2250°C. The test bars are characterized in Table 1.

Table 1

Ex No	Starck™ Powder	Binder (wt %)	%SiC/%C in Body	Cured Density (g/cm^3)	Firing Cond. (°C.)	Ceramic Density (g/cm^3)	4 pt MOR (kg/mm^2)
1	A	14	5.93/0.85		2100	4.27	41.9±4.3
2	A	14	5.93/0.85		2100	4.07	22.8±4.5
3	A	12.5	5.00/0.76		2100	3.98	19.9±2.9
4	A	13	5.47/0.78	2.87	2150	4.08	
					2100	4.13	
					2150*	4.17	23.5
					2250*	4.14	9.0
5	F	13	5.47/0.78	2.95	2150	4.22	
					2100	4.27	
					2150*	4.25	24.8
					2250*	4.14	10.2
6	A	13	4.65/2.13	2.99	2150	4.03	
					2100	4.18	38.3
					2150*	4.14	20.0
					2250*	4.18	9.8
7	F	13	4.65/2.13	2.96	2150	4.20	
					2100	4.24	37.0
					1900	3.99	
					2150*	4.27	29.1
					2250*	4.13	10.7
8	A	13	5.10/1.09	2.68	2150	3.98	40.1
					2100	4.16	43.7
					2150*	4.15	31.0
					2250*	4.13	11.4
9	F	13	5.10/1.09	2.62	2150	4.18	34.6
					2100	4.29	32.3
					2150*	4.26	15.4
					2250*	4.19	
10	A	20	8.8/1.1	2.75	2150	4.02	33.5
					2100	4.02	22.0
11	F	20	9.1/1.1	2.73	2150	4.25	26.4
					2100	4.10	17.9
12	A	13	6.9/0.8		2150*	4.15	37.1
					2250*	4.12	15.8
13	F	13	6.9/0.8		2150*	4.26	30.5
					2250*	4.17	14.8
14	A	12	4.2/2.5		2150*	3.88	19.1
					2250*	4.00	14.4
15	F	12	4.2/2.5		2150*	4.25	26.6
					2250*	4.25	14.1

* = 5.1 x 1.3 x 0.6 cm die

Claims

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of forming a handleable green body comprising:

(a) mixing components comprising titanium diboride powder and at least 10% by weight preceramic organosilicon polymer to a uniform mixture, wherein the preceramic organosilicon polymer is one which provides at least a stoichiometric amount of carbon based on the silicon content; and

(b) forming the uniform mixture into a desired shape to obtain said handleable green body.

2. A method of preparing a sintered ceramic body of titanium diboride comprising:

(a) preparing the handleable green body of claim 1; and

(b) sintering said body in an inert atmosphere at a temperature greater than 2000°C. to obtain a sintered body with a density greater than 4.0 g/cm^3.

3. The method of claim 2 wherein the preceramic organosilicon polymer is selected from polysiloxanes, polysilazanes, polysilanes and polycarbosilanes.

4. The method of claim 2 or claim 3 wherein at least one agent selected from curing agents and crosslinking agents is additionally present in the uniform mixture in an amount effective to crosslink the preceramic organosilicon polymer.

5. The method of claim 4 wherein the curing agent is selected from organic peroxides, which are present at 0.1 to 5.0 weight percent based on the weight of the preceramic organosilicon polymer or platinum-containing catalysts, which are present at 1.0 to 1000 ppm platinum based on the weight of the preceramic organosilicon polymer and the crosslinking agent comprises a siloxane with Si-H functional units.

6. The method of any one of claims 2 to 5 wherein the preceramic organosilicon polymer produces a char containing at least 10 wt% free carbon.

7. The method of any one of claims 2 to 6 wherein the handleable green body is sintered at a temperature between 2100 and 2250°C.

8. The method of any one of claims 3 to 7 wherein the preceramic organosilicon polymer is a polysiloxane comprising units selected from the group consisting of ($MeSiO_{1.5}$), ($MePhSiO$), ($PhSiO_{1.5}$), (Ph_2SiO), ($ViMe_2SiO$) and PhViSiO).

9. The method of any one of claims 3 to 7 wherein the preceramic organosilicon polymer is a polysilazane comprising units selected from the group consisting of [Ph_2SiNH], [$PhSi(NH)_{1.5}$], [$CH_2CH_2CH_2SiNH$] and combinations thereof.

10. The method of claim 1 wherein the titanium diboride powder has a number average particle size of less than 5 micrometers.

11. The method of any one of claims 2 to 9 wherein a processing aid selected from lubricants, deflocculants and dispersants is also present in the mixture.

12. A sintered titanium diboride body obtainable by the method of claim 2 comprising 2 to 10 wt% of silicon carbide, up to 3 wt% of boron carbide, up to 2 wt% of free carbon and 85 to 98 wt% of titanium diboride.

13. A method of preparing a handleable green body as defined in claim 1 as hereinbefore described in the description.

14. A handleable green body formed by the method of claim 1 or claim 13.

15. A method of preparing a sintered ceramic body of titanium diboride as hereinbefore described with reference to Examples 1 to 15 and Table 1.

16. A sintered titanium diboride body as hereinbefore described with reference to the Examples 1 to 15 and Table 1.

DATED this 9th day of February, 1998.
DOW CORNING CORPORATION

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

IAS:JGC:JL VAX doc 20 AU2720795.WPC

PREPARATION OF HIGH DENSITY TITANIUM DIBORIDE CERAMICS WITH PRECERAMIC POLYMER BINDERS

ABSTRACT

Disclosed is a method for preparing high density titanium diboride ceramic bodies. The method entails mixing titanium diboride powder with a preceramic organosilicon polymer. The mixture is then molded and sintered under pressure or by a pressureless process.