

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 January 2006 (12.01.2006)

PCT

(10) International Publication Number
WO 2006/004999 A1

(51) International Patent Classification⁷: C04B 35/565, 38/00, 41/51

(21) International Application Number:
PCT/US2005/023490

(22) International Filing Date: 30 June 2005 (30.06.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/584,244 30 June 2004 (30.06.2004) US

(71) Applicant (for all designated States except US): POCO GRAPHITE, INC. [US/US]; 300 Old Greenwood Road, Decatur, TX 76234 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): RASHED, Abuagela, H. [US/US]; 3220 Herring Court, Denton, TX 76210 (US). SHEPPARD, Rex, G. [US/US]; 102 Sendero, Decatur, TX 76234 (US). BRAY, Donald, J. [US/US]; 7712 Brookview Court, Irving, TX 75063 (US).

(74) Agents: RHEBERGEN, Constance, Gall et al.; Bracewell & Giuliani LLP, P.O. Box 61389, Houston, TX 77208-1389 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/004999 A1

(54) Title: A PROCESS FOR THE MANUFACTURING OF DENSE SILICON CARBIDE

(57) Abstract: A method of producing a densified SiC article is provided. Near-net shape porous silicon carbide articles are produced and densified using the developed method. A substantial number of pores within the porous near-net shape silicon carbide article are filled (impregnated) with a carbon precursor, a silicon carbide precursor, or a mixture of both. The carbon precursor can be liquid or gas. The filled SiC preform is heated to convert the carbon or silicon carbide precursor to porous carbon or SiC preform inside the pores of the net-shape silicon carbide article. The impregnation/pyrolysis cycle is repeated until the desired amount of carbon and/or silicon carbide is achieved. In case of a carbon or a mixture of silicon carbide/carbon precursor is used, the pyrolyzed near-net shape silicon carbide article is then contacted with silicon in an inert atmosphere. The silicon diffuses through the pyrolyzed near-net shape silicon carbide article and reacts with the carbon contained within the pores of the porous SiC preform producing a new phase of silicon carbide within the pores of the near-net shape silicon carbide article. The produced silicon carbide is a near-net dense silicon carbide article.

A PROCESS FOR THE MANUFACTURING OF DENSE SILICON CARBIDE

BACKGROUND OF THE INVENTION

Related Applications

This patent application claims priority to U.S. Provisional Patent Application Serial No. 60/584,244 filed on June 30, 2004, which is incorporated by reference in its entirety.

Technical Field of the Invention

[0001] The present invention relates to a method of producing silicon carbide articles.

Description of the Related Art

[0002] Silicon carbide (SiC) or moissanite is a ceramic compound consisting of carbon and silicon. SiC was accidentally discovered by Edward G. Acheson, an assistant to Thomas Edison, about 1890, when he was running an experiment on the synthesis of diamonds. Acheson thought the new material was a compound of carbon and alumina, present in the clay, leading him to name it carborundum, a name that is still being used on some occasions. SiC occurs naturally in meteorites, though very rarely and in very small amounts. Being the discoverer of SiC, Acheson was the first to synthesize SiC by passing an electric current through a mixture of clay and carbon. Today, SiC is still produced via a solid state reaction between sand (silicon dioxide) and petroleum coke (carbon) at very high temperatures in electric arc furnaces.

[0003] Several processes exist for making the SiC material. The most basic and simple process is combining sand and carbon in a temperature of about 1600 to 2500 °C. Other processes for the synthesis of SiC include chemical vapor deposition and pyrolysis of organic SiC precursors such as polycarbosilane polymers. Conventional processes for the fabrication of near-net shape dense SiC components such as pressureless sintering and hot pressing, and the like are difficult to operate and control and are cost-prohibitive.

[0004] Conventional ceramic processes, such as pressureless sintering, for the manufacturing of near-net shape SiC articles are becoming costly due to the increased complexity of some of these SiC components. To produce a SiC article, the starting SiC powder is processed in the form of dry powder or a slurry followed by shaping, 5 firing and final machining. The shaping or molding process requires the mold or die to be designed to accommodate for the shrinkage that takes place during the high temperature firing. The shrinkage of the SiC article is crucial to achieve the required densification or sintering. Accordingly, for every SiC article to be designed and manufactured, a special mold needs to be designed and made. Mold designs require 10 the knowledge of shrinkage behavior of the material, which is a function of the SiC particle size distribution, chemistry and rheology of the slurry, firing temperature, heating and cooling rates, etc. The effects of these parameters need to be determined experimentally until enough information is available for a suitable mold to produce a specific near-net shape SiC article. Furthermore, the mold has a limited lifetime due 15 to erosion resulting from each use that would cause dimensional changes of the mold, which in turn result in unpredictable dimensions of the sintered SiC product. In addition, producing a slurry with high solids loading and controlled chemistry and rheology requires the use of a bimodal SiC powder, where coarse particulates are mixed with fine powder. The use of coarse SiC particulates presents many problems 20 such as poor thermal shock resistance of the material and poor isotropy. Recent technical advances indicate that monolithic and composite materials with fine microstructure possess superior and more uniform properties.

[0005] Prior art processes for manufacturing dense SiC articles are difficult to operate and are expensive. A need exists for a process that is capable of producing SiC 25 articles that have reduced porosity to improve the chemical, mechanical, and thermal properties associated with SiC articles. It would be advantageous for the process to be simple to operate and be cost effective.

[0006] Recent studies have led to the development of a new SiC manufacturing process for the fabrication of near net shape SiC articles starting with near net shape 30 graphite articles. The new process is known as the chemical vapor reaction (CVR) process. The CVR process has the capability of producing very complex shapes of

SiC articles at a much lower cost than the conventional processes described above. However, SiC articles produced by the CVR process contain some porosity that could be detrimental to the chemical, mechanical and thermal properties of the SiC product. It would be advantageous to overcome this residual porosity. It would be
5 advantageous to convert such porosity into a second phase of SiC.

SUMMARY OF THE INVENTION

[0007] In view of the foregoing, the present invention advantageously provides a process for the manufacturing of dense, near-net shaped silicon carbide (SiC) articles having essentially no or substantially reduced porosity. The process described herein
10 densifies the porous, near-net shape SiC preform by converting the open porosity in the near-net shape SiC preform to a second phase of dense SiC.

[0008] As an embodiment of the present invention, a method of producing a densified SiC (silicon carbide) article is advantageously provided. In this embodiment, a porous SiC preform is provided. A preform is an article that can be formed to finish
15 form. In all embodiments of the present invention, the porous SiC preform can be formed starting with a graphite block that has an open porosity. The graphite block can be machined into a near-net shape graphite article. The term near-net shape is used here to indicate that the part will require only minimal post machining to meet final tolerances. The term preform encompasses near-net shape articles. The graphite
20 preform can then be contacted with silicon monoxide gas at a first preselected temperature to form the porous silicon carbide preform. A substantial number of pores within the porous silicon carbide preform are then filled with a carbon precursor to produce a filled silicon carbide preform. The filled silicon carbide preform is then heated at a second preselected temperature to polymerize the carbon precursor
25 contained within the filled silicon carbide preform to form a polymerized filled silicon carbide preform. The polymerized filled silicon carbide preform is further heated at a third preselected temperature to produce a carbonaceous porous structure within the pores of the porous silicon carbide preform. The carbonaceous porous structure, inside the SiC preform, is then contacted with silicon in an inert atmosphere at a
30 fourth preselected temperature and a first preselected pressure. In this step, the silicon

wicks through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform. The produced densified silicon carbide is characterized by having no or substantially reduced open porosity.

5 The elimination or substantial reduction in porosity will significantly improve most chemical, mechanical and thermal properties including but not limited to oxidation resistance, strength, stiffness, thermal conductivity, and thermal stability of SiC articles produced using the process described in this invention.

[0009] Variations to the processes described herein are possible. For example, in 10 embodiments of the present invention, the carbon precursor can be a liquid or a gas. Exemplary liquid carbon precursors can include a furfuryl alcohol, a liquid SiC-C precursor, or a phenolic resin. If a liquid carbon precursor is used, then the liquid carbon precursor can also include a catalyst and optionally a pore-forming agent. The catalyst can be a latent catalyst, an active catalyst, or a combination of both. In the 15 step of contacting the carbonaceous porous structure with silicon, the silicon can be a liquid or a gas. Other variations are possible as will be understood by those of ordinary skill in the art.

DETAILED DESCRIPTION OF THE INVENTION

[0010] As an embodiment of the present invention, a method of producing a densified 20 SiC article is advantageously provided. The resulting dense SiC article is created by converting the open porosity in the preform, or near-net shape, SiC article to a second phase of dense SiC. The porous SiC article, used as a preform, is produced using any of the different conventional processes for the manufacturing of porous ceramic bodies. Preferably, the preform SiC article is produced using the chemical vapor 25 reaction (CVR) process, as understood by those of ordinary skill in the art. The SiC preform preferably can contain an open porosity ranging from 10% to 60% by volume. In this process, the open pores are converted to a second phase of SiC.

[0011] In all embodiments that a porous silicon carbide preform is provided, the 30 porous silicon carbide structure can be produced by supplying a graphite block that has an open porosity. The graphite block is then machined into a near-net shape

article and then contacted with silicon monoxide gas at a first preselected temperature to form the porous silicon carbide preform. In all embodiments of the present invention, the first preselected temperature is in a range of about 1400°C to about 2000°C. The porous silicon carbide preform or SiC preform can be produced by other 5 methods as described herein.

[0012] A substantial number of pores within the porous silicon carbide preform are then filled with a carbon precursor to produce a filled silicon carbide preform. When the carbon precursor is a gas, the filled carbide preform has its pores at least partially filled with the gas. In this carbonization step, the carbon precursor impregnates or 10 infiltrates the porous silicon carbide preform to produce a carbon structure within the open pores of the porous silicon carbide preform. When the carbon precursor is liquid, the filled silicon carbide preform is then heated at a second preselected temperature to polymerize the carbon precursor contained within the filled silicon carbide preform to form a polymerized filled silicon carbide preform. In 15 embodiments of the present invention using a liquid precursor, the second preselected temperature is in a range of about 70°C to about 250°C. Another preferred embodiment includes the second preselected temperature being in a range of about 90 °C to about 150°C.

[0013] The polymerized filled silicon carbide structure is further heated at a third preselected temperature to produce a carbonaceous porous structure within the pores of the porous silicon carbide preform. The carbonaceous porous structure is essentially charred. In all embodiments of the present invention, the third preselected temperature is in a range of about 800 °C to about 1800 °C. In a preferred embodiment, the third preselected temperature is in a range of about 800 °C to about 25 1200 °C. The process can be repeated until the desired amount of carbon is produced within the pores of the porous SiC preform.

[0014] The carbonaceous porous structure is then contacted with silicon in an inert atmosphere at a fourth preselected temperature and a first preselected pressure. In 30 embodiments of the present invention contacting the carbonaceous porous structure with silicon in an inert atmosphere, the fourth preselected temperature is above about

a melting point of silicon. In this siliconization step, the silicon infiltrates or diffuses through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform. The produced silicon carbide is a near-net shape dense silicon carbide article. The conversion of carbon to SiC is accompanied with an increase in the molar volume which results in densification. The produced dense silicon carbide has essentially no or substantially reduced open porosity.

[0015] Variations to all embodiments of the processes described herein are possible. 10 For example, in embodiments of the present invention, the carbon precursor can be a liquid or a gas. Exemplary liquid carbon precursors can include a furfuryl alcohol, a liquid SiC-C precursor, or a phenolic resin. If a liquid carbon precursor is used, then the liquid carbon precursor can also include a catalyst and optionally a pore-forming agent. Example pore-forming agents can include diethylene glycol, polyethylene glycol, triethylene glycol, water, and combinations thereof. The catalyst can be a latent catalyst, an active catalyst, or a combination of both. In the step of contacting the carbonaceous porous structure with silicon, the silicon can be a liquid or a gas. Other variations are possible as will be understood by those of ordinary skill in the art.

[0016] When a pore-forming agent is used, it evaporates during the carbonization step 20 leaving behind a carbonaceous structure with interconnected open porosity. The selection of the pore-forming agent can allow for control of pore size distribution in the produced carbonaceous structure inside the pores of the SiC preform. If a liquid SiC-C precursor is used, a porous structure composed of a mixture of SiC and carbon will form during the carbonization step of the process when the filled SiC preform is 25 heated at a second preselected temperature. If a gaseous carbon precursor is used, then the heating step at the second pre-selected temperature can be excluded. The preferred gaseous carbon precursor dissociates at the third pre-selected temperature to deposit pyrolytic carbon/graphite inside the pores of the SiC article. Exemplary gaseous carbon precursors include most hydro-carbons such as methane and the like. 30 Alternatively, a liquid silicon carbide precursor can be used for the densification process. Exemplary SiC precursors include the liquid allylhydridopolycarbosilane

(AHPCS) and the like. When using a liquid silicon carbide precursor, , the final silicon infiltration step is optional, since there is no carbon that needs to be converted to SiC.

[0017] As another embodiment of the present invention, a method of producing a 5 densified SiC article is advantageously provided. In this embodiment, a porous silicon carbide preform having an open porosity is provided. The open porosity is preferably in a range of about 10% to about 60%. The porous silicon carbide preform can be formed or produced by supplying a graphite block having an open porosity, machining the graphite block into near-net shape graphite articles, and contacting the 10 near-net shape graphite article with silicon monoxide at a first preselected temperature to form a porous near-net shape silicon carbide preform or porous silicon carbide preform.

[0018] Other conventional manufacturing processes, such as SiC powder processing methods, can be used to form the porous silicon carbide preform.. Preferably, 15 however, the porous SiC preform is produced using the CVR process. In an example using the CVR process, the near-net shape porous SiC article is produced by supplying and machining a graphite block with known open porosity to produce a near-net shape graphite article. Several graphite grades are available with varying particle and pore size distribution characteristics. The near-net shape graphite article 20 is exposed to silicon monoxide (SiO) gas at high temperatures. The SiO gas diffuses throughout the graphite article and reacts with the graphite producing the porous SiC preform with minimal, predictable and constant dimensional increases. Other suitable processes for manufacturing the porous SiC preform will be known to those of skill in the art and are to be considered within the scope of the present invention.

25 [0019] A substantial number of pores within the porous silicon carbide preform are then filled with a liquid carbon precursor to produce a filled silicon carbide preform. The liquid carbon precursor further comprises a catalyst selected from the group consisting of a latent catalyst, an active catalyst, and combinations thereof. The filled silicon carbide preform is then heated at a second preselected temperature to 30 polymerize the liquid carbon precursor contained within the filled silicon carbide

5 preform to form a polymerized filled silicon carbide preform. The polymerized filled silicon carbide preform is then heated at a third preselected temperature to produce a carbonaceous porous structure within the pores of the porous silicon carbide preform. The carbonaceous porous structure is then contacted with silicon in an inert atmosphere at a fourth preselected temperature and a first preselected pressure. The silicon diffuses through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform.

10 [0020] As yet another embodiment of the present invention, the present invention advantageously includes a method of producing a densified SiC article having a near-net shape. In this embodiment, a porous silicon carbide preform having an open porosity is provided. The open porosity is preferably in a range of about 10% to about 60% porosity. The porous silicon carbide preform can be formed from a graphite block or other suitable manufacturing processes as described herein. The 15 preferred manufacturing method of producing the porous silicon carbide preform is utilizing the CVR process, as understood by those of ordinary skill in the art.

20 [0021] A substantial number of pores within the porous silicon carbide preform are filled with a gaseous carbon precursor that is allowed to diffuse throughout the porous silicon carbide preform and heated to a third pre-selected temperature to decompose the gaseous carbon precursor and deposit pyrolytic carbon/graphite within a substantial number of the pores of the porous silicon carbide preform to produce a filled silicon carbide preform. The filled silicon carbide preform is then contacted with silicon in an inert atmosphere at a temperature above the melting point of silicon and at a first preselected pressure. During this step, the silicon diffuses through the 25 carbonaceous porous structure and reacts with the pyrolytic carbon/graphite contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform. The resulting dense silicon carbide has essentially no or substantially reduced porosity.

EXAMPLE 1

A block of porous graphite was produced by Poco Graphite having an average porosity of about 30%. The porous graphite block was machined into 0.25"x2"x2" tiles and 0.25"x0.5"x4" bars. The porous graphite tiles and bars were then heated at 5 1800 °C in the presence of silicon monoxide gas to convert the porous graphite tiles and bars to porous silicon carbide tiles and bars. The porous silicon carbide tiles and bars were then impregnated with a liquid mixture of allylhydridopolycarbosilane (AHPCS) and phenolic resin which upon pyrolysis would produce a solid mixture of silicon carbide and carbon. The impregnated silicon carbide tiles and bars were then 10 heated to a pre-selected second temperature of 150 °C in air to polymerize the silicon carbide/carbon precursor. The tiles and bars were then heated further in an inert atmosphere to 1600 °C to char the polymer and to produce a mixture of silicon carbide and carbon structure inside the pores of the silicon carbide tiles and bars. This impregnation/polymerization/char cycle was repeated five more times to produce 15 more silicon carbide and carbon inside the pores of the silicon carbide tiles and bars. The carbonized tiles and bars were then infiltrated with liquid silicon at 1650 °C in an inert atmosphere. The liquid silicon filled the residual porosity of the tiles and bars and reacted with the carbon producing a new phase of silicon carbide. Characterization of the densified silicon carbide samples according to this example 20 resulted in the improved properties shown by Table 1.

EXAMPLE 2

A block of porous graphite was produced by Poco Graphite having an average porosity of about 30%. The porous graphite block was machined into 0.25"x2"x2" and 0.25"x4"x4" porous graphite tiles. The graphite tiles were then heated at 1800 °C 25 in the presence of silicon monoxide gas to convert the graphite tiles to silicon carbide tiles. The porous silicon carbide tiles were then impregnated with a liquid mixture of catalyzed furfuryl alcohol as the carbon precursor and a mixture of diethylene glycol and triethylene glycol as the pore-forming agent. The impregnated silicon carbide tiles were then heated to 90 °C in air to polymerize the furfuryl alcohol. The samples 30 were then further heated in an inert atmosphere to 1000 °C to evaporate the pore-forming agent and char the polymer to produce a carbon structure with interconnected

porosity inside the pores of the silicon carbide tiles. This carbonization cycle was repeated one more time to produce more carbon inside the pores of the silicon carbide tiles. The carbonized tiles were then infiltrated with liquid silicon at 1650 °C in an inert atmosphere. The liquid silicon filled the residual porosity of the tiles and reacted 5 with the carbon producing a new phase of silicon carbide. The dense silicon carbide tiles were then machined into test specimens for measuring their physical, thermal and mechanical properties. Table 1 shows the results.

EXAMPLE 3

A block of porous graphite was produced by Poco Graphite having an average 10 porosity of about 30%. The porous graphite block was machined into 0.25"x2"x2" tiles and 0.25"x0.5"x4" bars. The graphite tiles and bars were then heated at 1800 °C in the presence of silicon monoxide gas to convert the graphite tiles and bars to silicon carbide tiles and bars. The porous silicon carbide tiles and bars were then heated to about 1000 °C in the presence of methane (CH₄) gas as the carbon precursor. The 15 methane gas diffused into the pores and decomposed into solid pyrolytic carbon/graphite and hydrogen gas. The solid carbon/graphite deposited inside the pores of the silicon carbide tiles and bars while the hydrogen gas diffused out of the porous silicon carbide tiles and bars. This process was allowed to continue until the samples gained about 4-5% weight. The carbonized tiles and bars were then 20 infiltrated with liquid silicon at 1650 °C in inert atmosphere to convert the pyrolytic carbon/graphite to silicon carbide.

EXAMPLE 4

A block of porous graphite was produced by Poco Graphite having an average 25 porosity of about 30%. The porous graphite block was machined into 0.25"x2"x2" tiles and 0.25"x0.5"x4" bars. The porous graphite tiles and bars were then heated at 1800 °C in the presence of silicon monoxide gas to convert the porous graphite tiles and bars to porous silicon carbide tiles and bars. The porous silicon carbide tiles and bars were then impregnated with the commercially available liquid AHPSCS as the 30 silicon carbide precursor. The impregnated silicon carbide tiles and bars were then heated to about 150 °C in air to polymerize the silicon carbide precursor. The tiles and bars were then heated further in an inert atmosphere to 1600 °C to pyrolyze the

polymer and convert it to SiC preform inside the pores of the silicon carbide tiles and bars. This impregnation/polymerization/pyrolysis cycle was repeated five more times to produce more silicon carbide inside the pores of the silicon carbide tiles and bars. No silicon infiltration was necessary in this example. Characterization of the 5 densified silicon carbide samples according to this example resulted in improved properties as shown by Table 1.

Table 1. Some Properties of the Densified Silicon Carbide as Compared to the Porous Silicon Carbide Preform.

Property	SiC Preform	Example 1	Example 2	Example 4
Density (g/cm ³)	2.53	3.08	3.05	2.71
Open Porosity (%)	18-19	0.3	0.2	2.3
Total Impurity (ppm)	5	14	6	30
Flexural Strength (ksi)	21.3	27.1	39.0	29.7
Young's Modulus (msi)	33	58	55	35
Fracture Toughness, K _{IC} (MPa·m ^{1/2})	2.25	N/A	2.84	N/A
Thermal Conductivity (W/m·K)	157	N/A	218	165

10 [0022] As an advantage of the present invention, the SiC articles made in accordance with an embodiment of the present invention have improved chemical, mechanical, and thermal properties, such as improved resistance to oxidation, increased strength, improved stiffness, improved thermal conductivity, and improved thermal stability. As another advantage of the present invention, neither the carbonization step nor the 15 siliconization step results in significant overall dimensional change in the porous silicon carbide preform. Because the overall size of the article is not changed significantly, the required post machining is minimum to produce the final net shape dense SiC articles which reduces the manufacturing cost as compared to other conventional prior art processes for the production of dense SiC article.

[0023] While the invention has been shown or described in only some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes without departing from the scope of the invention. For example, various means of contacting the porous silicon carbide preform with the carbon precursor can be used or various methods of producing the carbon preform can be used. In addition, other types of pore-forming agents can be used when a liquid carbon precursor is used.

CLAIMS

We claim:

1. A method of producing a densified SiC article, the method comprising the steps of:
 - 5 a) supplying a porous SiC preform having an open porosity;
 - b) filling a substantial number of pores within the porous silicon carbide preform with a carbon precursor to produce a filled silicon carbide preform; and
 - c) heating the filled silicon carbide preform at a third preselected temperature to produce a carbonaceous porous structure within the pores of the porous silicon carbide preform such that the resulting densified SiC article exhibits lower porosity than the porous SiC preform.
- 10 2. The process of claim 1, further comprising the step of contacting the carbonaceous porous structure with silicon in an inert atmosphere at a fourth preselected temperature and a first preselected pressure so that the silicon diffuses through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform.
- 15 3. The process as described in claim 2, wherein the fourth preselected temperature is above about the melting point of silicon.
- 20 4. The process as described in claim 2, wherein the step of contacting the carbonaceous porous structure with silicon includes utilizing silicon selected from the group consisting of a gas and a liquid.

5. The process as described in claim 2, wherein the first preselected pressure is selected from the group consisting of atmospheric pressure, high pressure, vacuum, or partial vacuum.
6. The process as described in any of the preceding claims, wherein the carbon precursor is a gaseous carbon precursor that is allowed to diffuse throughout the porous silicon carbide preform.
7. The process as described in any of the preceding claims, further comprising the step of heating the filled silicon carbide preform at a second preselected temperature to polymerize the carbon precursor contained within the filled silicon carbide preform such that the filled silicon carbide preform is a polymerized filled silicon carbide preform.
8. The process as described in claim 7, wherein the second preselected temperature is in a range of 70 °C to about 250 °C.
9. The process as described in any of the preceding claims, wherein the carbon precursor comprises a liquid carbon precursor.
10. The process as described in claim 9, wherein the liquid carbon precursor comprises a furfuryl alcohol.
11. The process as described in claim 9, wherein the liquid carbon precursor further comprises a catalyst selected from the group consisting of a latent catalyst, an active catalyst, and combinations thereof;
12. The process as described in claim 9, wherein the liquid carbon precursor further comprises a pore-forming agent selected from the group consisting of diethylene glycol, polyethylene glycol, triethylene glycol, water, and combinations thereof and a

catalyst selected from the group consisting of a latent catalyst, an active catalyst, and combinations thereof.

13. The process as described in claim 9, wherein the liquid carbon precursor is selected from the group consisting of a liquid SiC-C precursor.

5 14. The process as described in any of the preceding claims, wherein the third preselected temperature is in a range of about 800 °C to about 1800 °C.

15. The process as described in any of the preceding claims, wherein the step of supplying a porous silicon carbide preform includes the steps of:

- a) supplying a graphite block having an open porosity.
- 10 b) machining the graphite block into near-net shape graphite articles; and
- c) contacting the near-net shape graphite article with silicon monoxide at a first preselected temperature to form a porous silicon carbide preform.

16. The process as described in claim 15, wherein the first preselected temperature is in a range of about 1400 °C to about 2000 °C.

15 17. The process as described in claim 15, wherein the graphite block has an open porosity of about 10% to about 60% porosity.

18. A method of producing a densified SiC article, the method comprising the steps of:

- a) supplying a porous SiC preform having an open porosity;
- 20 b) filling a substantial number of pores within the porous silicon carbide preform with a liquid carbon precursor to produce a filled silicon carbide preform, the

liquid carbon precursor further comprising a catalyst selected from the group consisting of a latent catalyst, an active catalyst, and combinations thereof;

5 c) heating the filled silicon carbide preform at a second preselected temperature to polymerize the liquid carbon precursor contained within the filled silicon carbide preform to form a polymerized filled silicon carbide preform; and

d) heating the polymerized filled silicon carbide preform at a third preselected temperature to produce a carbonaceous porous structure within the pores of the porous silicon carbide preform.

19. The process as described in claim 18, further comprising the step of contacting the
10 carbonaceous porous structure with silicon in an inert atmosphere at a fourth preselected temperature and a first preselected pressure so that the silicon diffuses through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform.

15 20. The process as described in any of the preceding claims, wherein the liquid carbon precursor is selected from the group consisting of a liquid SiC-C precursor.

21. The process as described in any of the preceding claims, wherein the step of contacting the carbonaceous porous structure with silicon includes utilizing silicon selected from the group consisting of a gas and a liquid.

20 22. A method of producing a densified SiC article, the method comprising the steps of:

- a) supplying a porous SiC preform having an open porosity;
- b) filling a substantial number of pores within the porous silicon carbide preform with a gaseous carbon precursor that is allowed to diffuse throughout the porous silicon carbide preform;

- c) heating the filled SiC preform at a third pre-selected temperature to decompose the gaseous carbon precursor and deposit pyrolytic carbon within the pores of the porous silicon carbide preform to produce a filled silicon carbide preform; and
- 5 d) contacting the carbonized porous SiC preform with silicon in an inert atmosphere at a temperature about above the melting point of silicon and at a first preselected pressure so that the silicon diffuses through the carbonaceous porous structure and reacts with carbon contained within the pores of the porous silicon carbide preform to produce silicon carbide within the pores of the porous silicon carbide preform.

10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/023490

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C04B35/565 C04B38/00 C04B41/51																
According to International Patent Classification (IPC) or to both national classification and IPC																
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C04B																
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX																
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left; padding: 2px;">Category °</th> <th style="text-align: left; padding: 2px;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="text-align: left; padding: 2px;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 2px;">Y</td> <td style="text-align: left; padding: 2px;">US 6 221 475 B1 (DOMERGUE JEAN-MARC ET AL) 24 April 2001 (2001-04-24) column 9, lines 34-58; claim 11; examples 1-4 -----</td> <td style="text-align: center; padding: 2px;">1-14, 18-22</td> </tr> <tr> <td style="text-align: center; padding: 2px;">Y</td> <td style="text-align: left; padding: 2px;">EP 0 956 276 B (SOCIETE NATIONALE D'ETUDE ET DE CONSTRUCTION DE MOTEURS D'AVIATION SNE) 3 December 2003 (2003-12-03) paragraphs '0065! - '0067!; claim 11; examples 1,3,4 -----</td> <td style="text-align: center; padding: 2px;">1-14, 18-22</td> </tr> <tr> <td style="text-align: center; padding: 2px;">A</td> <td style="text-align: left; padding: 2px;">DE 101 43 015 A1 (DEUTSCHES ZENTRUM FUER LUFT- UND RAUMFAHRT E.V) 27 March 2003 (2003-03-27) the whole document -----</td> <td style="text-align: center; padding: 2px;">1,18,22</td> </tr> <tr> <td style="text-align: center; padding: 2px;">-----</td> <td style="text-align: center; padding: 2px;">-/-</td> <td style="text-align: center; padding: 2px;">-----</td> </tr> </tbody> </table>		Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US 6 221 475 B1 (DOMERGUE JEAN-MARC ET AL) 24 April 2001 (2001-04-24) column 9, lines 34-58; claim 11; examples 1-4 -----	1-14, 18-22	Y	EP 0 956 276 B (SOCIETE NATIONALE D'ETUDE ET DE CONSTRUCTION DE MOTEURS D'AVIATION SNE) 3 December 2003 (2003-12-03) paragraphs '0065! - '0067!; claim 11; examples 1,3,4 -----	1-14, 18-22	A	DE 101 43 015 A1 (DEUTSCHES ZENTRUM FUER LUFT- UND RAUMFAHRT E.V) 27 March 2003 (2003-03-27) the whole document -----	1,18,22	-----	-/-	-----
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.														
Y	US 6 221 475 B1 (DOMERGUE JEAN-MARC ET AL) 24 April 2001 (2001-04-24) column 9, lines 34-58; claim 11; examples 1-4 -----	1-14, 18-22														
Y	EP 0 956 276 B (SOCIETE NATIONALE D'ETUDE ET DE CONSTRUCTION DE MOTEURS D'AVIATION SNE) 3 December 2003 (2003-12-03) paragraphs '0065! - '0067!; claim 11; examples 1,3,4 -----	1-14, 18-22														
A	DE 101 43 015 A1 (DEUTSCHES ZENTRUM FUER LUFT- UND RAUMFAHRT E.V) 27 March 2003 (2003-03-27) the whole document -----	1,18,22														
-----	-/-	-----														
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.																
<input checked="" type="checkbox"/> Patent family members are listed in annex.																
° Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed																
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family																
Date of the actual completion of the international search	Date of mailing of the international search report															
24 October 2005	03/11/2005															
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Vathilakis, S															

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/023490

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	<p>WANG Y ET AL: "The fabrication of reaction-formed silicon carbide with controlled microstructure by infiltrating a pure carbon preform with molten Si" CERAMICS INTERNATIONAL, ELSEVIER, AMSTERDAM, NL, vol. 30, no. 3, 2004, pages 435-439, XP004494749 ISSN: 0272-8842 the whole document</p> <p>-----</p> <p>WANG Y ET AL: "The effect of porous carbon preform and the infiltration process on the properties of reaction-formed SiC" CARBON, vol. 42, no. 8-9, 2004, pages 1833-1839, XP004509643 ISSN: 0008-6223 the whole document</p> <p>-----</p>	1,18,22
P,A		1,18,22

INTERNATIONAL SEARCH REPORT

Information on patent family members

 International Application No
PCT/US2005/023490

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6221475	B1	24-04-2001	AT	255545 T		15-12-2003
			CA	2268516 A1		23-04-1998
			CN	1237950 A		08-12-1999
			DE	69726604 D1		15-01-2004
			DE	69726604 T2		30-09-2004
			EP	0835853 A1		15-04-1998
			WO	9816484 A1		23-04-1998
			HK	1023984 A1		27-08-2004
			JP	2001505863 T		08-05-2001
			KR	2000049126 A		25-07-2000
			RU	2201542 C2		27-03-2003
EP 0956276	B	03-12-2003	EP	0956276 A1		17-11-1999
DE 10143015	A1	27-03-2003		NONE		