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REINFORCED CERAMIC MATRIX  
COMPOSITES****Publication Classification**(51) **Int. Cl.**  
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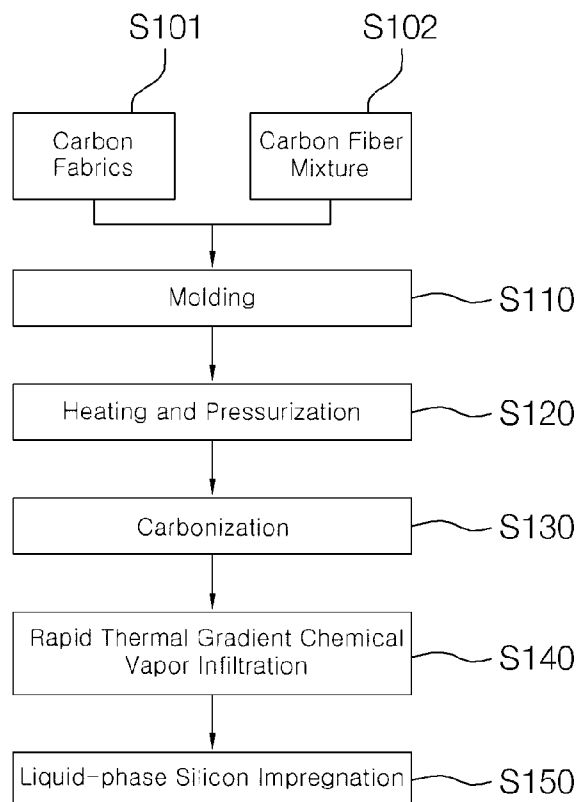
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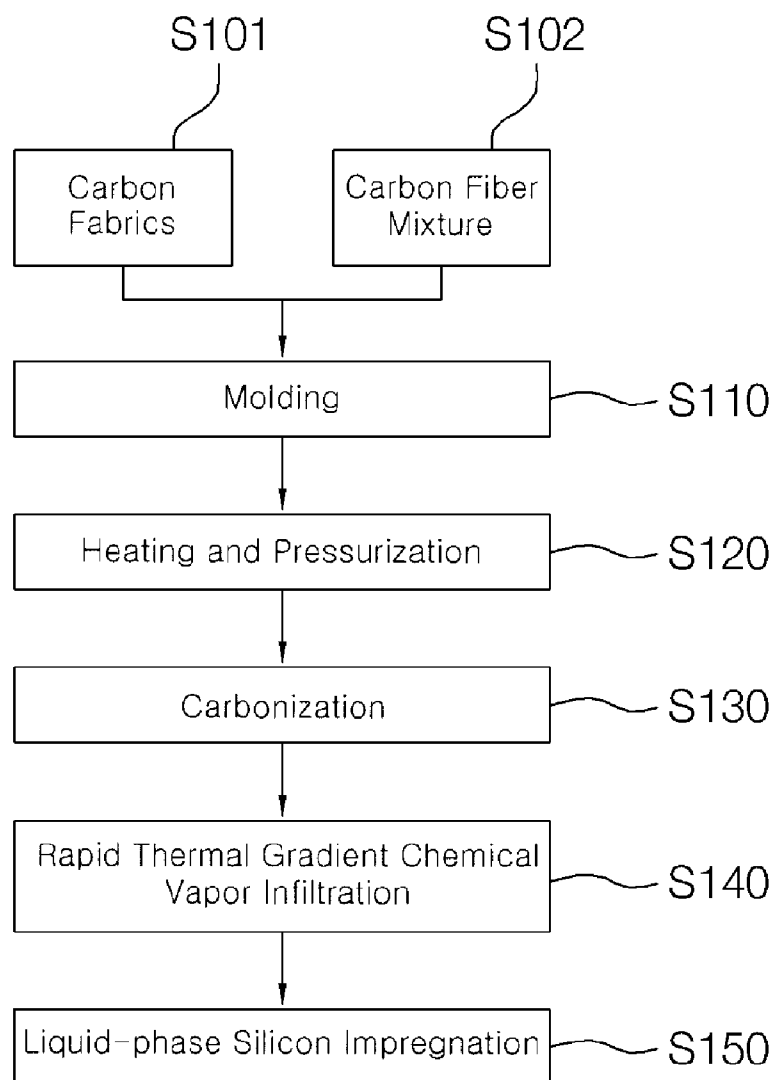
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(57) **ABSTRACT**

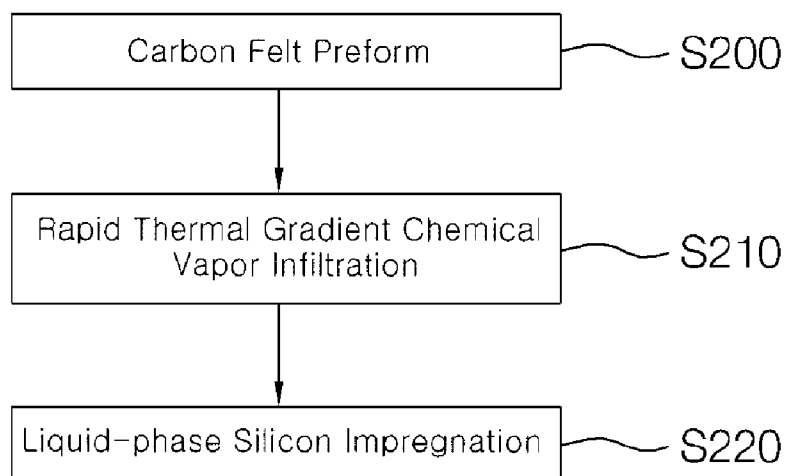
The present invention relates to a method of producing carbon fiber reinforced ceramic matrix composites, the method of producing carbon fiber reinforced ceramic matrix composites according to the present invention is characterized in that the method comprises the steps of: producing a carbon fiber reinforced resin composite that is molded with a mixture in which carbon fibers and polymer precursors containing carbon are mixed; producing a carbon fiber reinforced carbon composite by depositing pyrolytic carbon during a rapid thermal gradient chemical vapor infiltration process while increasing the deposition speed in a direction from the inside to the outside by performing a thermal treatment on said carbon fiber reinforced resin composite at high temperature; and infiltrating liquid-phase silicon into the pores of said carbon fiber reinforced carbon composite. The method of producing carbon fiber reinforced ceramic matrix composites according to the present invention as described above has the effect of improving the properties of carbon fiber reinforced ceramic matrix composites, and it is possible to deposit a pyrolytic carbon layer at a deposition speed 5-10 times faster than other conventional chemical vapor infiltration processes, thereby showing a remarkably improved effect in terms of manufacturing process, time, and cost.



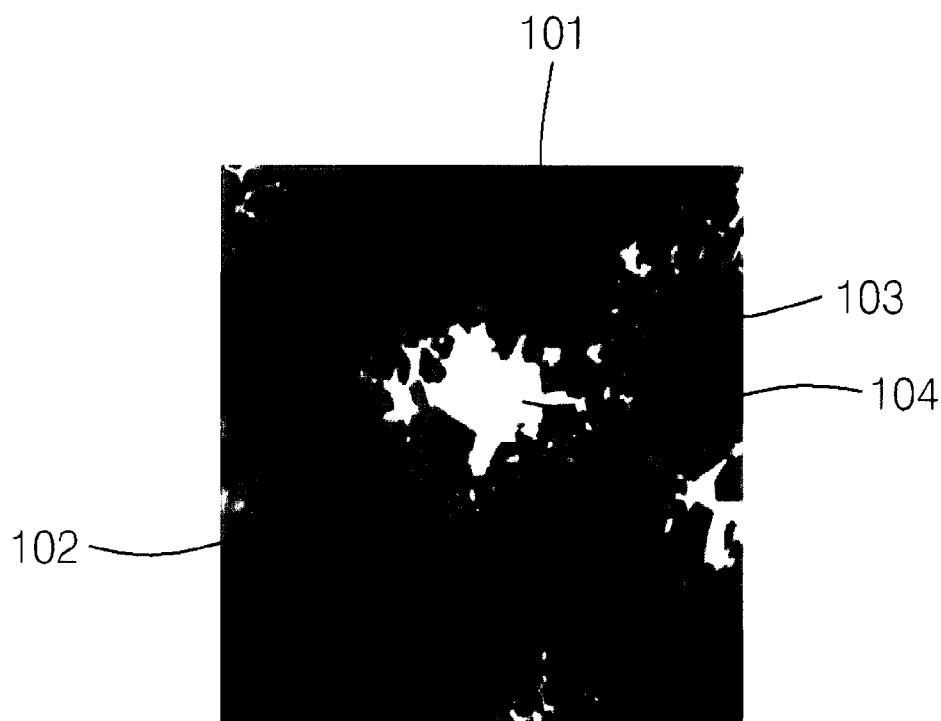
[Fig. 1]



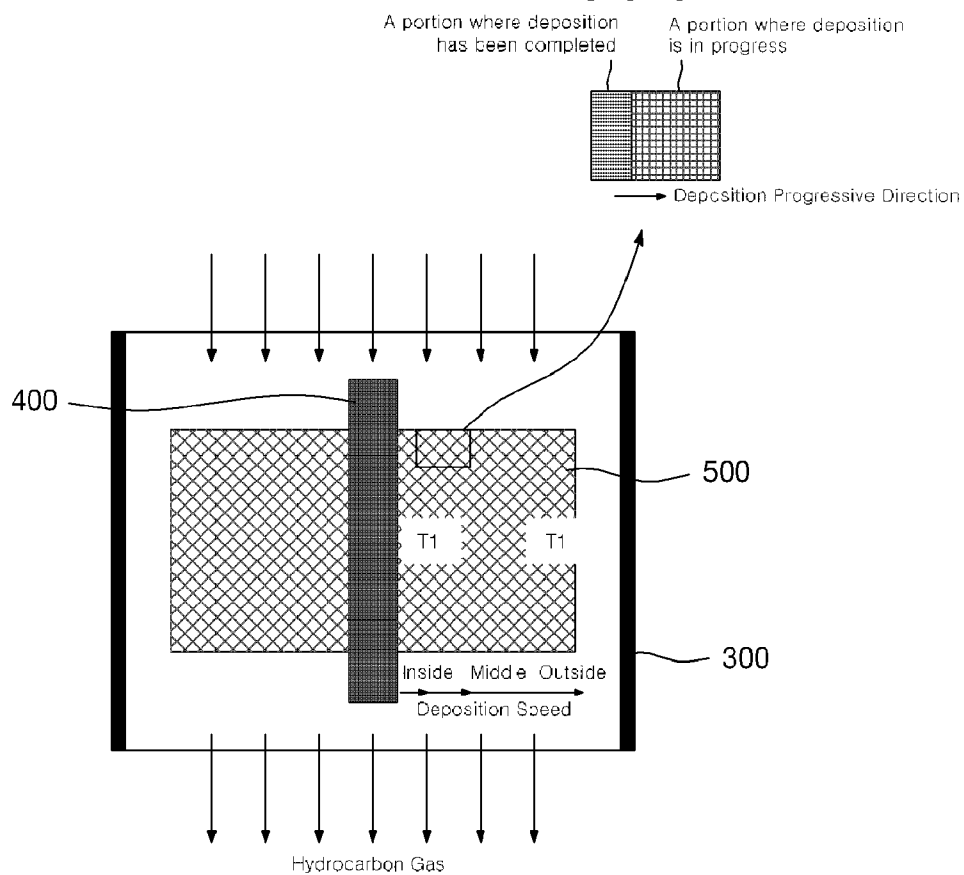
[Fig. 2]



[Fig. 3]



[Fig. 4]



## METHOD OF PRODUCING CARBON FIBER REINFORCED CERAMIC MATRIX COMPOSITES

### TECHNICAL FIELD

**[0001]** The present invention relates to a method of producing carbon fiber reinforced ceramic matrix composites, maintaining excellent mechanical strength at high temperature as well as having excellent properties in corrosion resistance, thermal resistance, friction and abrasion under a severe environment, such as heat, chemical erosion, etc.

### BACKGROUND ART

**[0002]** Fiber reinforced ceramic matrix composites are lightweight materials having excellent mechanical and thermal properties at high temperature. With these properties, fiber reinforced ceramic matrix composites are applicable to friction and abrasion materials, such as brake disks, and pads for aircraft or ground transport means, and also to ultrahigh thermal resistant materials, such as ceramic engines, and rocket nozzle parts, which require mechanical strength, corrosion resistance, and thermal resistance. Fiber reinforced ceramic matrix composites have been studied to overcome the drawbacks to monolithic ceramics, such as brittle failure, or the like, and they can be produced by filling the pores of a preform made of carbon fibers or silicon carbide fibers with thermal resistant materials, such as pyrolytic carbon, silicon carbide, or boron nitride.

**[0003]** Up to now, fiber reinforced ceramic matrix composites have been produced with a variety of manufacturing processes, however, in most cases, they cause mechanical and/or chemical impact damages to fibers during the manufacturing processes. To solve such a problem, ceramic matrix composites are produced by injecting precursors in a gas state into a porous fiber preform having low density, and then pyrolyzing it for the deposition of ceramic matrix-phase. Such a process is called chemical vapor in-filtration, and the matrix-phase is infiltrated under a low temperature and pressure condition during this manufacturing process to solve the problem causing damage to fibers, which has been created when producing conventional ceramic matrix composites.

**[0004]** In this process, however, high-priced raw materials and manufacturing equipment are employed, its manufacturing process is complicated, and lots of process time more than several hundred hours is required, and therefore its application is extremely restricted to high-tech industries, such as aerospace, or the like.

**[0005]** Rather than the chemical vapor infiltration process using raw materials in a gas state, a process of producing carbon fiber reinforced ceramic matrix composites by infiltrating liquid-phase silicon into a porous carbon preform has been developed.

**[0006]** As described in U.S. Pat. No. 6,308,808, U.S. Pat. No. 6,358,565, and U.S. Pat. No. 5,942,064 owned by Walter Krenkel et al., a mixture including carbon fibers that have been cut out, liquid-phase phenol, and carbon powder, is molded under a high temperature and pressure condition, and then a thermal treatment process at high temperature is performed to produce a carbon fiber reinforced carbon composite. The produced carbon fiber reinforced carbon composite is infiltrated with liquid-phase silicon to produce a carbon fiber reinforced ceramic matrix composite, and it is applicable to brake disks for ground vehicles and thermal resistance materials in the field of aerospace.

**[0007]** As described above, however, the carbon fiber reinforced resin composite produced by mixing with liquid-phase

carbon precursors is more effective than existing chemical vapor infiltration processes in terms of manufacturing cost, but it is difficult to prevent the reaction of liquid-phase silicon against carbon fibers due to some difficulties in forming a uniform carbon fiber protective layer, and thereby rapidly reducing mechanical properties of carbon fiber reinforced ceramic matrix composites. To solve such a problem, as disclosed in Korean Patent Application No. 1999-7008146, as well as U.S. Pat. No. 6,079,525, U.S. Pat. No. 6,030,913, and U.S. Pat. No. 6,231,791, the carbon fiber reinforced ceramic matrix composite is produced by iterative impregnation of liquid organic binders or by changing the composition of the mixture, but it is impossible to prevent the reduction in mechanical properties caused by carbon fiber erosion and to improve friction and abrasion characteristics at high temperature.

**[0008]** As a different process from the above, as disclosed in U.S. Pat. No. 6,221,475 and Korean Patent Application No. 1999-7003211, a preform made of weaved carbon fibers is deposited with pyrolytic carbon by means of an isothermal/isobaric chemical vapor infiltration (ICVI) process, and then a densification process is performed on carbon precursors by means of a liquid-phase infiltration method to produce a carbon fiber reinforced ceramic matrix composite. This process has remarkably improved an aspect of fiber protection, but it is difficult to produce carbon fiber reinforced ceramic matrix composites having a complicated shape due to difficulty in combining different carbon fiber reinforced ceramic matrix composites into a structured body. In particular, the manufacturing process is complicated and required more than several hundred hours for the manufacturing time, and therefore it caused an increase in the manufacturing cost.

**[0009]** Examining the overall problems related to the production technologies of carbon fiber reinforced ceramic matrix composites in most cases a process of producing a carbon fiber reinforced carbon composite that is employed for producing carbon fiber reinforced ceramic matrix composites still has some difficulties in terms of its production cost and technologies. For example, conventional chemical vapor infiltration process has excellent characteristics as a fiber protective layer; but it is not adequate for producing carbon fiber reinforced carbon composites due to its high-cost raw materials and manufacturing process difficulties. Furthermore, when carbon fiber reinforced resin composites are produced by performing an infiltration process of organic binders containing carbon component, it is known that iterative infiltration processes are required, and the effect is reduced in an aspect of fiber protection.

### DISCLOSURE OF INVENTION

#### Technical Problem

**[0010]** The present invention is devised to solve the aforementioned problems, and it is an object of the invention to provide a method of producing carbon fiber reinforced ceramic matrix composites for improving thermal and mechanical properties of the carbon fiber reinforced ceramic matrix composites and for providing a solution to the problems due to its high manufacturing cost and processes as described above, by improving the method of producing starting material and a carbon fiber reinforced carbon composite, which are required for producing the carbon fiber reinforced ceramic matrix composites.

**[0011]** To solve the above problems, a method of producing carbon fiber reinforced ceramic matrix composites is provided by the inventors to simplify the manufacturing process by employing a carbon felt preform having a sandwich struc-

ture or a carbon fiber mixture as starting material, and to produce carbon fiber reinforced carbon composites having a uniform fiber protective layer with a rapid and low cost process by applying a rapid thermal gradient chemical vapor infiltration process as well as employing a liquid-phase silicon infiltration process.

#### Technical Solution

**[0012]** To achieve the aforementioned object, a method of producing carbon fiber reinforced ceramic matrix (C/C—SiC) composites according to the present invention comprises the steps of: producing a carbon fiber reinforced resin composite that is molded with a mixture in which carbon fibers and polymer precursors containing carbon are mixed; producing a carbon fiber reinforced carbon composite by depositing pyrolytic carbon during a rapid thermal gradient chemical vapor infiltration process while increasing the deposition speed in a direction from the inside to the outside by performing a thermal treatment on said carbon fiber reinforced resin composite at high temperature; and infiltrating liquid-phase silicon into the pores of said carbon fiber reinforced carbon composite.

**[0013]** Moreover, it is preferable that the mixture includes 10-60 wt % of the carbon fibers, and 30-60 wt % of the polymer precursors containing carbon.

**[0014]** Further, it is preferable that the mixture includes less than 30 wt % silicon carbide powder, and less than 30 wt % carbon powder.

**[0015]** Further, it is preferable that the carbon fiber reinforced resin composite is stacked with the mixture and carbon fabrics alternately.

**[0016]** Further, it is preferable that the green body is formed with a first surface layer for preventing carbon fibers from reacting with silicon by means of the mixture that has been mixed during the mixing process, and the first surface layer is formed with a ceramic matrix layer including silicon carbide and silicon by chemically reacting with the liquid-phase silicon in the step of infiltrating the liquid-phase silicon.

**[0017]** Further, it is preferable that the green body undergoes a thermal treatment in a range of 900-2,200° C. under inert gas atmosphere, and then a pyrolytic carbon matrix layer as a second surface layer is deposited on the first surface layer in a deposition step through the rapid thermal gradient chemical vapor infiltration process.

**[0018]** Further, it is preferable that the deposition step by the rapid thermal gradient chemical vapor infiltration process is performed in a range of pyrolytic reaction temperatures 700-1,200° C. and reaction pressures 188-1,130 torr using hydro-carbon gas.

**[0019]** Further, it is preferable that a deposition region is divided into a plurality of regions from the inside to the outside, and individual regions are deposited at different speeds one another in a deposition step through the rapid thermal gradient chemical vapor infiltration process.

**[0020]** Further, it is preferable that the deposition region is deposited from the inside to the outside at a deposition speed in a range of 0.5-3.0 mm/hr.

**[0021]** Further, it is preferable that the carbon fiber reinforced carbon composite has 1.0-1.7 g/cm<sup>3</sup> apparent density, and 5-30% of open pores that are used for infiltrating paths of the liquid-phase silicon.

**[0022]** Further, it is preferable that the step of infiltrating liquid-phase silicon is performed by stacking the carbon fiber reinforced carbon composite on silicon powder, maintaining a pressure less than 100 torr within a reactor, and then heating it at the silicon melting point more than 1,410° C., thereby

infiltrating liquid-phase silicon into a preform while chemically reacting with a plurality of carbon layers.

**[0023]** To achieve the aforementioned object, a method of producing carbon fiber reinforced ceramic matrix composites according to the present invention is characterized in that the method comprises the steps of: producing a carbon felt preform; producing a carbon fiber reinforced carbon composite by depositing the carbon felt preform through a rapid thermal gradient chemical vapor infiltration process while increasing the deposition speed from the inside to the outside; and infiltrating liquid-phase silicon into the pores of the carbon fiber reinforced carbon composite.

**[0024]** Moreover, it is preferable that the carbon felt preform is any one of carbon-based fibers, such as oxyphene, phene, rayon, pitch-based, etc.

**[0025]** Further, it is preferable that the carbon felt preform has mat laminates with quasi-isotropic orientations, such as 0/+60/-60°, and it is reinforced with carbon fibers less than 10 mm in the Z-direction.

**[0026]** Further, it is preferable that the carbon felt preform is deposited with a pyrolytic layer having 5-100  $\mu$ m thickness by means of a deposition step through the rapid thermal gradient chemical vapor infiltration process.

**[0027]** Further, it is preferable that carbon fibers are reinforced in the three X, Y and Z axes by impregnating liquid-phase silicon into the carbon fiber reinforced carbon composite in the step of infiltrating liquid-phase silicon.

**[0028]** Further, it is preferable that the deposition step by the rapid thermal gradient chemical vapor infiltration process is performed in a range of pyrolytic reaction temperatures 700-1,200° C. and reaction pressures 188-1,130 torr using hydro-carbon gas.

**[0029]** Further, it is preferable that a deposition region is divided into a plurality of regions from the inside to the outside, and individual regions are deposited at different speeds one another in a deposition step through the rapid thermal gradient chemical vapor infiltration process.

**[0030]** Further, it is preferable that the deposition region is deposited from the inside to the outside at a deposition speed in a range of 0.5-3.0 mm/hr.

**[0031]** Further, it is preferable that the carbon fiber reinforced carbon composite has 1.0-1.7 g/cm<sup>3</sup> apparent density, and 5-30% of open pores that are used for infiltrating paths of the liquid-phase silicon.

**[0032]** Further, it is preferable that the step of infiltrating liquid-phase silicon is performed by stacking the carbon fiber reinforced carbon composite on silicon powder, maintaining a pressure less than 100 torr within a reactor, and then heating it at the silicon melting point more than 1,410° C., thereby infiltrating liquid-phase silicon into the carbon felt preform while chemically reacting with a plurality of carbon layers.

#### ADVANTAGEOUS EFFECTS

**[0033]** The method of producing carbon fiber reinforced ceramic matrix composites according to the present invention as shown above has the effect of improving the properties of carbon fiber reinforced ceramic matrix composites, and it is possible to deposit a pyrolytic carbon layer at a deposition speed 5-10 times faster than other conventional chemical

vapor infiltration processes, thereby providing a remarkably improved effect in terms of manufacturing process, time, and cost.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0034] FIG. 1 is a block diagram illustrating a method of producing carbon fiber reinforced ceramic matrix composites using carbon fabrics and a carbon fiber mixture according to the present invention.

[0035] FIG. 2 is a block diagram illustrating a method of producing carbon fiber reinforced ceramic matrix composites using a carbon felt preform according to the present invention.

[0036] FIG. 3 is a microscopic structural view of a carbon fiber reinforced ceramic matrix composite according to the present invention.

[0037] FIG. 4 is a conceptual view illustrating a rapid thermal gradient chemical vapor in-filtration process according to the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0038] Hereinafter, a method of producing carbon fiber reinforced ceramic matrix composites will be described. The method of forming and producing each of mixture in the following embodiments can be implemented in a variety of ways by modifying a part of the composition. However, if any technical elements claimed by the present invention are basically included in the modified embodiments, they should be considered to be within the technical scope of the invention.

[0039] First, in view of starting material, a carbon felt preform reinforced with carbon fibers in the direction of three X, Y, and Z axes may be employed, or a sandwich structure that is produced by stacking a mixture comprising carbon fibers 0.3-150 mm in length, polymer precursors containing carbon, silicon carbide powder, and graphite powder with carbon fabrics alternately may be applied, or a carbon fiber reinforced resin composite (CFRP) comprising only the aforementioned mixture may be employed.

[0040] Moreover, pyrolytic carbon is deposited on the produced starting material by means of a rapid thermal gradient chemical vapor infiltration process to produce a porous carbon fiber reinforced carbon composite, and then liquid-phase silicon is infiltrated into the pores of the carbon fiber reinforced carbon composite to produce a carbon fiber reinforced ceramic matrix composite. The carbon fiber reinforced ceramic matrix composites has physical properties of more than 2.2 g/cm<sup>2</sup> apparent density, less than 1% apparent porosity, more than 100 MPa bending strength, and more than 35 W/mk thermal conductivity.

[0041] The method of producing carbon fiber reinforced ceramic matrix composites can be divided into two types of processes based upon its starting material as shown in FIG. 1 and FIG. 2.

[0042] First, FIG. 1 illustrates a process for producing a carbon fiber reinforced resin composite using a mixture comprising carbon fibers cut in the size of 0.3-150 mm, polymer precursors containing carbon, silicon carbide powder, and graphite powder with carbon fabrics.

[0043] In the step of producing a carbon fiber reinforced resin composite, carbon fibers cut in the size of 0.3-150 mm is added to distilled water together with polymer precursors containing carbon, silicon carbide powder, graphite powder,

and carbon fabrics to produce a uniform mixture through dispersion and mixing processes.

[0044] Furthermore, this mixture will be formed with a first surface layer comprising polymer precursors containing carbon, silicon carbide powder, and graphite powder on a carbon fiber surface, whose mixture ratio is 10-60 wt % carbon fibers, 30-60 wt % polymer precursors containing carbon. In addition, silicon carbide powder and carbon powder will be included selectively. In other words, it may be composed of 0-30 wt % silicon carbide powder, and 0-30 wt % carbon powder (S101 and S102).

[0045] The mixture produced in this way is alternately stacked with carbon fabrics to form a green body having a sandwich structure (S110). The carbon fabrics may be formed with plain, satin, and twill weaves. Here, for another method, the green body, may be produced by stacking only the mixture, without stacking carbon fabrics alternately.

[0046] Subsequently, the produced green body is placed in a mold, and then heated and pressurized simultaneously in a range of 80-250° C. and 1-20 MPa to produce a carbon fiber reinforced resin composite. At this time, the produced carbon fiber reinforced resin composite has physical properties of apparent density 1.2-1.6 g/cm<sup>2</sup>, and apparent porosity 1-20% (S110, S120 and S130).

[0047] For the aforementioned method of producing carbon fiber reinforced ceramic matrix composites, technical specifications disclosed in Korean Patent Application Nos. 1995-0069130 and 1997-0023344 filed by this applicant, may be employed for applying to other embodiments.

[0048] Subsequently, in the deposition step by means of a rapid thermal gradient chemical vapor infiltration process (S140), the produced carbon fiber reinforced resin composite is subjected to thermal treatment in a range of 700-2,200° C. under inert gas atmosphere, and then a rapid thermal gradient chemical vapor infiltration process is performed to produce a carbon fiber reinforced carbon composite.

[0049] More specifically, the rapid thermal gradient chemical vapor infiltration process according to the present invention is provided to produce a carbon fiber reinforced carbon composite having high density greater than 1.3 g/cm<sup>3</sup>, and this rapid thermal gradient chemical vapor infiltration process performs a rapid deposition by dividing a region to be deposited into three or more portions to control its deposition speed for each portion. Here, deposition speed is controllable by moving a thermocouple that has been installed in a chemical vapor deposition apparatus to increase the speed gradually in the green body from the inside to the outside.

[0050] In other words, as illustrated in FIG. 4, a carbon fiber reinforced resin composite 500 is installed in a reactor, and a heating element 400 is installed in the center. Furthermore, it may be implemented by supplying hydrocarbon gas as a process gas. In addition, deposition speed is controllable by using a thermocouple (not shown) as described above, and the deposition process may be performed from the inside to the outside.

[0051] Moreover, for deposition speed arrows as illustrated in the drawing, a shorter one indicates a low deposition speed, and a longer one indicates a high deposition speed. Furthermore, the T1 and T2 portions denote a high temperature and a low temperature respectively, and thereby a thermal gradient will be induced.

[0052] Here, deposition speed will be within a range of 0.5-3.0 mm/hr, and it will be deposited from the inside to the outside. For example, a region can be divided into three

portions, such as the inside, the middle, and the outside, and then they may be deposited at 1.0 mm/hr, 1.5 mm/hr, and 2.0 mm/hr respectively to perform a deposition process more rapidly. Here, deposition speed is set to be low in the inside portion, because the deposition in the inside will be relatively slower than the outside.

**[0053]** When deposition speed is controlled in this manner, its manufacturing process and cost may be greatly improved and cut down, compared to all other existing chemical vapor infiltration processes, such as isothermal/isobaric chemical vapor infiltration process, pressure gradient chemical vapor infiltration process, and existing isokinetic thermal gradient chemical vapor infiltration process, which require lots of manufacturing cost due to their complicated process and long manufacturing time.

**[0054]** This rapid thermal gradient chemical vapor infiltration process may be performed at a deposition speed 10 times faster and more densely than the thermal gradient chemical vapor infiltration process disclosed in Korean Patent No. 0198154 owned by this applicant to form a pyrolytic carbon layer approximately 5-100  $\mu$ m in thickness.

**[0055]** Additionally, the pyrolytic carbon layer that has been formed at this time will act as a reaction layer to form silicon carbide matrix-phase by reacting with liquid-phase silicon during the liquid-phase silicon impregnation process.

**[0056]** The carbon fiber reinforced resin composite that has been produced by the rapid thermal gradient chemical vapor infiltration process according to the present invention has physical properties of apparent density 1.0-1.7 g/cm<sup>3</sup>, and apparent porosity 5-30%.

**[0057]** Then, the carbon fiber reinforced carbon composite produced by the rapid thermal gradient chemical vapor infiltration process is placed on silicon powder having particles in a range of 1  $\mu$ m-10 mm in size during a liquid-phase silicon infiltration process.

**[0058]** Here, as a process condition, it is heated at a silicon melting point greater than 1,410° C. under vacuum atmosphere. Most of pores existing within the carbon fiber reinforced carbon composite will be filled with the silicon that has been melted at high temperature above 1,410° C. by capillary action of the pores in a few minutes, and at the same time it will be reacted with a carbon reaction layer on carbon fibers to form a silicon carbide. In this way, the finally produced carbon fiber reinforced ceramic matrix composite is composed of 30-60 wt % carbon, 35-60 wt % silicon carbide, and less than 5 wt % non-reaction silicon.

**[0059]** Next, the carbon fiber reinforced ceramic matrix composite can be produced using a green body made of a carbon felt preform as starting material as illustrated in FIG. 2.

**[0060]** First, a carbon felt preform reinforced in the three X, Y and Z axes is produced (S200); more specifically, carbon-based fibers, such as oxyphene, phene, rayon, pitch-based, or the like are wound around a mandrel to produce unidirectional carbon mats, and the carbon mats produced by this method are stacked together. For its stacking method, they are alternately stacked with quasi-isotropic orientation at 0/+60/-60°.

**[0061]** Furthermore, at least two layers may be stacked, and then punched using a needle to reinforce all layers in the z-direction, and the above process will be reiterated to produce a felt preform greater than 30 mm in thickness.

**[0062]** This felt preform is made by a fiber volume ratio approximately 10-55%, where the thickness of one layer is

approximately less than 0.1 mm, the length of fabrics in length is less than 10 mm, and the fabric ratio is approximately 10%. Furthermore, a needle having density of 15 penetration/cm<sup>2</sup> may be used for the Z-direction.

**[0063]** Then, in order to remove impurities of the carbon felt preform, a thermal treatment process is performed at a temperature greater than 1,700° C. under vacuum atmosphere. The method of producing such a carbon felt preform is disclosed in the embodiments of U.S. patent application Ser. No. 10/180,778 and the Korean Patent No. 27788, filed by this applicant.

**[0064]** Subsequently, a carbon fiber reinforced carbon composite is produced by means of a rapid thermal gradient chemical vapor infiltration process (S210). The same rapid thermal gradient chemical vapor infiltration process as in the embodiment of the aforementioned first process will be applied to this.

**[0065]** In addition, a carbon fiber reinforced ceramic matrix composite is produced by means of a liquid-phase silicon infiltration process (S220). The same liquid-phase silicon infiltration process as in the embodiment of the aforementioned first process will be applied to this.

## MODE FOR THE INVENTION

### First Embodiment

**[0066]** A mixture comprising 30 wt % carbon fibers that have been cut out in the size of 30 mm, 40 wt % phenol resin, 5 wt % carbon powder, and 5 wt % silicon carbide powder is prepared and stacked alternately with carbon fabrics in the form of 20 wt % satin weave to produce a green body. The produced green body is placed in a mold, and then cured while being pressurized at a pressure 2 MPa for 10 minutes to produce a carbon fiber reinforced resin composite.

**[0067]** The carbon fiber reinforced resin composite is subjected to thermal treatment in inert gas atmosphere. Furthermore, pyrolytic carbon is deposited in a condition of rapid thermal gradient chemical vapor infiltration process to produce a carbon fiber reinforced carbon composite.

**[0068]** The produced carbon fiber reinforced carbon composite is stacked on silicon powder, and heated at 1,550° C. in vacuum atmosphere, and infiltrated with liquid-phase silicon to produce a carbon fiber reinforced ceramic matrix composite. Here, physical properties of the produced carbon fiber reinforced ceramic matrix composite are shown in Table 1.

### Second Embodiment

**[0069]** A mixture comprising 55 wt % carbon fibers that have been cut out in the size of 30 mm, 35 wt % phenol resin, 5 wt % carbon powder, and 5 wt % silicon carbide powder is prepared to produce a green body. Stacking alternately with carbon fabrics is not implemented in the second embodiment. The produced green body is placed in the mold, and then cured while being pressurized at a pressure 2 MPa for 10 minutes to produce a carbon fiber reinforced resin composite.

**[0070]** The carbon fiber reinforced resin composite is subjected to thermal treatment in inert gas atmosphere. Furthermore, pyrolytic carbon is deposited in a condition of rapid thermal gradient chemical vapor infiltration process to produce a carbon fiber reinforced carbon composite.

**[0071]** The produced carbon fiber reinforced carbon composite is stacked on silicon powder, and heated at 1,550° C. in vacuum atmosphere, and infiltrated with liquid-phase silicon to produce a carbon fiber reinforced ceramic matrix composite.

ite. Here, physical properties of the produced carbon fiber reinforced ceramic matrix composite are shown in Table 1.

### Third Embodiment

**[0072]** 320K oxyphene carbon fiber is wound around a mandrel to produce unidirectional carbon mats, and the carbon mats produced by this method are stacked together. For stacking method, they are stacked alternately by a method of 0/+60/-60°.

**[0073]** At least two layers are stacked together, and then punched using a needle to reinforce every layer in the z-direction, and the process is reiterated to produce a felt preform having 30 mm in thickness. This felt preform is produced at approximately 45% of oxyphene fiber volume ratio, where the thickness of a layer is approximately 0.9 mm, and the fiber ratio in the z-direction is approximately 10%.

**[0074]** The produced preform is subjected to thermal treatment at 1,700° C. in vacuum atmosphere to remove the impurities of the preform.

**[0075]** Pyrolytic carbon is deposited on the produced carbon felt preform in a condition of rapid thermal gradient chemical vapor infiltration process to produce a carbon fiber reinforced carbon composite.

**[0076]** The produced carbon fiber reinforced carbon composite is stacked on silicon powder and heated at 1,550° C. in vacuum atmosphere, and infiltrated with liquid-phase silicon to produce a carbon fiber reinforced ceramic matrix composite. Here, the physical properties of the produced carbon fiber reinforced ceramic matrix composite are shown in Table 1.

### Comparative Example 1

**[0077]** A mixture is prepared by mixing 54 wt % of carbon fibers that have been cut out in the size of 130 mm, 36 wt % of phenol resin, and 10 wt % of carbon powder, and is placed in a mold, and then cured while being pressurized at 3 MPa of pressure to produce a carbon fiber reinforced resin composite.

**[0078]** The carbon fiber reinforced resin composite is subjected to thermal treatment at 900° C. in inert gas atmosphere to produce a carbon fiber reinforced carbon composite. The produced carbon fiber reinforced carbon composite is stacked on silicon powder and heated at 1,600° C. in vacuum atmosphere, and infiltrated with liquid-phase silicon to produce a carbon fiber reinforced ceramic matrix composite. Here, the physical properties of the produced carbon fiber reinforced ceramic matrix composite are shown in Table 1.

TABLE 1

| Specimen              | Apparent Density<br>g/cm <sup>3</sup> | Apparent Porosity<br>(%)<br>% | Bending Strength<br>MPa | Thermal Conductivity<br>W/mK | Friction Factor |
|-----------------------|---------------------------------------|-------------------------------|-------------------------|------------------------------|-----------------|
| First Embodiment      | 2.3                                   | 0.5                           | 125                     | 40                           | 0.45            |
| Second Embodiment     | 2.4                                   | 0.3                           | 120                     | 42                           | 0.45            |
| Third Embodiment      | 2.3                                   | 0.7                           | 140                     | 40                           | 0.43            |
| Comparative Example 1 | 2.1                                   | 0.9                           | 80                      | 35                           | 0.40            |

**[0079]** As described above, for a method of producing carbon fiber reinforced ceramic matrix composites according to the present invention, carbon fibers in the carbon fiber reinforced carbon composites, which have been produced by the rapid thermal gradient chemical vapor infiltration process, have a uniformly deposited pyrolytic carbon layer, and such a

pyrolytic carbon layer is reacted with silicon to form silicon carbide during the liquid-phase silicon impregnation process. The pyrolytic carbon layer has excellent properties for a fiber protection layer to prevent carbon fiber erosion, which is a most difficult problem during the liquid-phase silicon permeation process, as well as for a reaction layer to form silicon carbide; moreover, it improves physical properties of carbon fiber reinforced ceramic matrix composites by forming a new interface between carbon fibers and silicon carbide matrix-phase.

**[0080]** The microstructure of carbon fiber reinforced ceramic matrix composites that have been produced by the production method according to the present invention comprises a pyrolytic carbon layer **102** as shown in a dark gray portion, a silicon carbide layer **103** as shown in a light gray portion, and a residual silicon layer **104** as shown in the lightest color portion. It is known that carbon fiber erosion is hardly created by the pyrolytic carbon layer around carbon fibers, and silicon carbide is formed around the pyrolytic carbon layer.

**[0081]** Furthermore, for a rapid thermal gradient chemical vapor infiltration process according to the present invention in terms of the time of producing carbon fiber reinforced ceramic matrix composites, pyrolytic carbon layer can be deposited at a deposition speed 10 times faster or more than conventional chemical vapor infiltration processes, or 5 times faster or more than conventional thermal gradient chemical permeation processes, thereby remarkably reducing the cost of producing carbon fiber reinforced carbon composites.

**[0082]** Moreover, carbon fiber reinforced resin composites can be simply produced by one-time process without performing iterative densification processes that are typically employed in the process of producing carbon fiber reinforced resin composites using liquid-phase precursors containing carbon. In addition, in combination with the rapid thermal gradient chemical vapor infiltration process and the liquid-phase silicon impregnation process, it is possible to simplify the process of producing carbon fiber reinforced ceramic matrix composites, thus reducing its manufacturing cost remarkably, and therefore application of carbon fiber reinforced ceramic matrix composites to a variety of industry fields is possible.

**[0083]** Furthermore, for a green body that has been produced by mixing carbon fibers in the size of 0.3-150 mm with polymer precursors containing carbon, silicon carbide powder, and graphite powder, and then alternatively stacking with carbon fabrics, or that has been produced by the mixture only, its dispersion and mixture is uniform, and also it has excellent properties for forming a first surface layer of carbon fibers and carbon fabrics. Additionally, as contraction is hardly generated when it is subjected to thermal treatment at a high temperature greater than 1,000° C., there are no dimensional changes, thus reducing the cost of processing its dimension and shape remarkably.

### INDUSTRIAL APPLICABILITY

**[0084]** The present invention is applicable to the transportation industry, such as aerospace, or ground vehicles.

1. A method of producing carbon fiber reinforced ceramic matrix composites comprising the steps of:

producing a carbon fiber reinforced resin composite that is molded with a mixture in which carbon fibers and polymer precursors containing carbon are mixed;

producing a carbon fiber reinforced carbon composite by depositing pyrolytic carbon during a rapid thermal gradient chemical vapor infiltration process while increasing the deposition speed in a direction from the inside to



the outside by performing a thermal treatment on said carbon fiber reinforced resin composite at high temperature; and

infiltrating liquid-phase silicon into the pores of said carbon fiber reinforced carbon composite.

2. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein said mixture includes 10-60 wt % of said carbon fibers, and 30-60 wt % of said polymer precursors containing carbon.

3. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 2, wherein said mixture includes less than 30 wt % silicon carbide powder, and less than 30 wt % carbon powder.

4. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 2 or 3, wherein said carbon fiber reinforced resin composite is stacked with said mixture and carbon fabrics alternately.

5. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 4, wherein said green body is formed with a first surface layer for preventing carbon fibers from reacting with silicon by means of said mixture that has been mixed during the mixing process, and said first surface layer is formed with a ceramic matrix layer including silicon carbide and silicon by chemically reacting with said liquid-phase silicon in the step of infiltrating said liquid-phase silicon.

6. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein said green body undergoes a thermal treatment in a range of 900-2,200° C. in inert gas atmosphere, and then a pyrolytic carbon matrix layer as a second surface layer is deposited on the first surface layer in a deposition step through said rapid thermal gradient chemical vapor infiltration process.

7. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein the deposition step by said rapid thermal gradient chemical vapor infiltration process is performed in a range of pyrolytic reaction temperatures 700-1,200° C. and reaction pressures 188-1,130 torr using hydro-carbon gas.

8. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein a deposition region is divided into a plurality of regions from the inside to the outside, and individual regions are deposited at different speeds from one another in a deposition step through said rapid thermal gradient chemical vapor infiltration process.

9. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein said deposition region is deposited from the inside to the outside at a deposition speed in a range of 0.5-3.0 mm/hr.

10. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein said carbon fiber reinforced carbon composite has 1.0-1.7 g/cm<sup>3</sup> apparent density, and 5-30% of open pores that are used for infiltrating paths of said liquid-phase silicon.

11. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 1, wherein the step of infiltrating liquid-phase silicon is performed by stacking said carbon fiber reinforced carbon composite on silicon powder, maintaining a pressure less than 100 torr within a reactor, and then heating it at the silicon melting point more than 1,410° C., thereby infiltrating liquid-phase silicon into a preform while chemically reacting with a plurality of carbon layers.

12. A method of producing carbon fiber reinforced ceramic matrix composites comprising the steps of:

producing a carbon felt preform;

producing a carbon fiber reinforced carbon composite by depositing said carbon felt preform through a rapid thermal gradient chemical vapor infiltration process while increasing the deposition speed from the inside to the outside; and

infiltrating liquid-phase silicon into the pores of said carbon fiber reinforced carbon composite.

13. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein said carbon felt preform is any one of carbon-based fibers, such as oxyphene, phene, rayon, pitch-based, etc.

14. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein said carbon felt preform has mat laminates with quasi-isotropic orientations, such as 0/+60/-60°, and it is reinforced with carbon fibers less than 10 mm in the Z-direction.

15. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein said carbon felt preform is deposited with a pyrolytic layer having 5-100  $\mu$ m thickness by means of a deposition step through said rapid thermal gradient chemical vapor infiltration process.

16. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein carbon fibers are reinforced in the three X, Y and Z axes by impregnating liquid-phase silicon into said carbon fiber reinforced carbon composite in the step of infiltrating liquid-phase silicon.

17. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein the deposition step by said rapid thermal gradient chemical vapor infiltration process is performed in a range of pyrolytic reaction temperatures 700-1,200° C. and reaction pressures 188-1,130 torr using hydro-carbon gas.

18. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein a deposition region is divided into a plurality of regions from the inside to the outside, and individual regions are deposited at different speeds from one another in a deposition step through said rapid thermal gradient chemical vapor infiltration process.

19. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein said deposition region is deposited from the inside to the outside at a deposition speed in a range of 0.5-3.0 mm/hr.

20. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein said carbon fiber reinforced carbon composite has 1.0-1.7 g/cm<sup>3</sup> apparent density, and 5-30% of open pores that are used for infiltrating paths of said liquid-phase silicon.

21. The method of producing carbon fiber reinforced ceramic matrix composites according to claim 12, wherein the step of infiltrating liquid-phase silicon is performed by stacking said carbon fiber reinforced carbon composite on silicon powder, maintaining a pressure less than 100 torr within a reactor, and then heating it at the silicon melting point more than 1,410° C., thereby infiltrating liquid-phase silicon into a carbon felt preform while chemically reacting with a plurality of carbon layers.

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