



(51) International Patent Classification:

B32B 18/00 (2006.01) C04B 35/185 (2006.01)

C04B 35/117 (2006.01) C04B 35/626 (2006.01)

C04B 35/18 (2006.01) C04B 35/80 (2006.01)

(21) International Application Number:

PCT/US2018/043476

(22) International Filing Date:

24 July 2018 (24.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: SIEMENS AKTIENGESELLSCHAFT [DE/DE]; Werner-von-Siemens-Straße 1, 80333 München (DE).

(71) Applicant (for BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW only): SIEMENS ENERGY, INC. [US/US]; 4400 Alafaya Trail, Orlando, Florida 32826-2399 (US).

(72) Inventors: MORRISON, Jay A.; 2885 Kingfisher Way, Mims, Florida 32754 (US). MERRILL, Gary B.; 847 Post Lane, Orlando, Florida 32804 (US). LAMPENSCHERF, Stefan; Cheruskerweg 8, 85586 Poing (DE). PHAM, Gia Khanh; Blumenweg 44, 85579 Neubiberg (DE).

(74) Agent: SCOTT, Mark W.; Siemens Corporation- Intellectual Property Dept., 3501 Quadrangle Blvd Ste 230, Orlando, Florida 32817 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

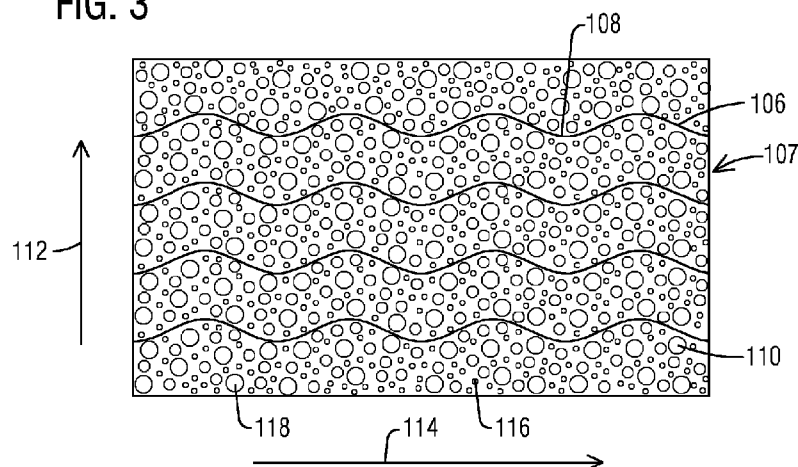
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: CERAMIC MATRIX COMPOSITE MATERIALS HAVING REDUCED ANISOTROPIC SINTERING SHRINKAGE

FIG. 3



(57) Abstract: There are provided ceramic matrix composite structures (100) and processes for making the same that reduce anisotropic sintering shrinkage via the ceramic particles (100, 116, 118, 120) utilized for the matrix portion of the ceramic matrix composite structure (100). Ceramic particles of two different sizes with a difference in size of a factor of 100 are impregnated into the plurality of fiber layers.

CERAMIC MATRIX COMPOSITE MATERIALS HAVING REDUCED ANISOTROPIC SINTERING SHRINKAGE

FIELD

5 The present disclosures relates to high temperature ceramic matrix composite materials, and more particularly to ceramic matrix composite (CMC) materials which reduce a shrinkage differential (Δ) in an in-plane vs. through thickness direction (anisotropic sintering shrinkage) therein, and to methods for making the same.

10

BACKGROUND

Gas turbines comprise a casing or cylinder for housing a compressor section, a combustion section, and a turbine section. A supply of air is compressed in the compressor section and directed into the combustion
15 section. The compressed air enters the combustion inlet and is mixed with fuel. The air/fuel mixture is then combusted to produce high temperature and high pressure (working) gas. This working gas then travels past the combustor transition piece and into the turbine section of the turbine.

Generally, the turbine section comprises rows of vanes which direct the
20 working gas to the airfoil portions of the turbine blades. The working gas travels through the turbine section, causing the turbine blades to rotate, thereby turning the rotor. The rotor is also attached to the compressor section, thereby turning the compressor and an electrical generator for producing electricity. High efficiency of a combustion turbine is achieved by
25 heating the gas flowing through the combustion section to as high a temperature as is practical. The hot gas, however, may degrade the various metal turbine components, such as the combustor, transition ducts, vanes, ring segments, and turbine blades that it passes when flowing through the turbine.

30 For this reason, strategies have been developed to protect turbine components from extreme temperatures, such as the development and

selection of high temperature materials adapted to withstand these extreme temperatures and cooling strategies to keep the components adequately cooled during operation. State of the art superalloys with additional protective coatings are commonly used for hot gas path components of gas turbines. In view of the substantial and longstanding development in the area of superalloys, however, it figures to be extremely difficult to further increase the temperature capability of superalloys.

Accordingly, ceramic matrix composite (CMC) materials have been developed with greater temperature resistance relative to superalloys. Such CMC materials include a ceramic or a ceramic matrix material, either of which hosts a plurality of reinforcing fibers. Typically, the ceramic or ceramic matrix material is impregnated or otherwise infiltrated into an existing reinforcing fiber matrix (e.g., a woven matrix or the like) and is sintered (heat treated) at a temperature effective to ensure flow of the ceramic/ceramic matrix material into the fiber material and dry/stabilize the resulting ceramic matrix composite material. The ceramic/ceramic matrix and fibers are typically formed from either an oxide or non-oxide material (e.g., carbides, nitrides). When both the matrix and fibers both comprise oxide materials, they are typically referred to as "oxide-oxide" materials.

In the manufacture of the ceramic matrix composite, the matrix will shrink, primarily in a through thickness direction. In contrast, however, the fibers of the reinforcing fiber matrix are already fully sintered prior to CMC processing and thus have very little shrinkage during sintering. Typically, the ceramic or ceramic matrix shrinkage is at least ten times that of the fibers. As a result, there is a significant differential between in plane shrinkage vs. the through thickness shrinkage for standard CMC materials. This differential (also referred to as "anisotropic sintering shrinkage" leads to defects (e.g., voids and cracks) in the CMC material and even poorer interlaminar strength upon being subjected to the high temperatures associated with gas turbine operation. This is especially of concern since CMC materials are already known to have poor interlaminar strength.

For components having a relatively flat profile (e.g., plates), high anisotropic sintering shrinkage results in matrix cracking oriented perpendicular to the orientation of the fiber material. For complex shapes, such as at airfoil leading and trailing edges, while the anisotropic sintering shrinkage may be less in the perpendicular orientation, such anisotropic sintering shrinkage results in interlaminar defects parallel to fabric plane. An example of a turbine component having interlaminar cracking as a result of such differential shrinkage is in FIG. 7. These defects further weaken the already low interlaminar properties of the CMC and severely limit design capabilities.

Several solutions have been proposed in the art to eliminate defects caused by anisotropic sintering shrinkage. For example, particles (e.g., mullite) that result in less anisotropic sintering shrinkage have been proposed. However, CMC materials resulting from such particles have been found to have further reduced matrix and CMC interlaminar strengths. In another proposed solution, high local compaction pressures are applied to the CMC structure during drying, particularly with stacked laminates or fillets that make up the airfoil. This may be done utilizing hard tooling or the like. The effect is that matrix rich zones are reduced in size and therefore limit the size of defects from sintering shrinkage. However, this approach is difficult to carry out with complex shapes and reproducibility is challenging. Moreover, such processes are inconsistent with high volume production methods such as autoclaving, which displace high cost hard tooling. Accordingly, there is a need for processes and materials that reduce anisotropic sintering shrinkage and the effects thereof in CMC materials.

SUMMARY

Aspects of the present invention are directed to CMC components and methods of making the same that reduce anisotropic sintering shrinkage via optimization of the particles utilized to prepare the matrix portion of the CMC material. By the terms "matrix or matrix portion," it is meant the materials

(ceramic or ceramic matrix material) constituting the portion of the CMC material aside from the reinforcing fiber material. In accordance with an aspect, anisotropic sintering shrinkage is reduced or eliminated herein via the presence and use of ceramic particles which provide a through thickness shrinkage that more closely approaches an in plane shrinkage for the subject CMC material.

Thus, in accordance with one aspect, there is provided a process for making a ceramic matrix composite structure. The process comprises:

impregnating a fiber material comprising a plurality of layers of ceramic fibers with a medium comprising a plurality of ceramic particles to form an impregnated fiber material, wherein the particles comprise at least first ceramic particles and second ceramic particles, the second ceramic particles having an average diameter less than an average diameter of the first ceramic particles;

sintering the impregnated fiber material to produce the ceramic matrix composite structure;

wherein the process comprises utilizing first ceramic particles and second ceramic particles of an average particle size in the impregnating step effective to provide a through thickness shrinkage of 1.0 % (0.01) or less for the impregnated fiber material during the sintering step, wherein the through thickness shrinkage is determined according to the formula:

$$S = t/R$$

wherein R = the average diameter of the first ceramic particles;

wherein S = the through thickness shrinkage of the impregnated fiber material; and

wherein t = the average diameter of the second ceramic particles.

In accordance with another aspect, there is provided another process for making a ceramic matrix composite structure. The process comprises:

impregnating a fiber material comprising a plurality of layers of ceramic fibers with a medium comprising a plurality of ceramic particles, wherein the particles comprise at least first ceramic particles and second ceramic

particles, the second ceramic particles having an average diameter less than an average diameter of the first ceramic particles;

sintering the impregnated fiber material to produce the ceramic matrix composite structure;

5 wherein the process comprises utilizing first ceramic particles and second ceramic particles of an average particle size in the impregnating step effective to provide a through thickness shrinkage during the sintering which is at least (within) 50% of an in plane shrinkage for the ceramic matrix composite structure upon the sintering.

10 In accordance with another yet aspect, there is provided a ceramic matrix composite structure. The structure comprises:

a fiber material comprising plurality of layers of ceramic fibers;

an impregnated fiber material comprising a fiber material impregnated with a medium comprising a plurality of ceramic particles;

15 wherein the ceramic particles comprise at least first ceramic particles and second ceramic particles, the second ceramic particles having an average diameter less than an average diameter of the first ceramic particles; and

20 wherein an average diameter of the first ceramic particles and the second ceramic particles is effective to provide a through thickness shrinkage which is at least (within) 50% of an in plane shrinkage for the impregnated fiber material upon sintering of the impregnated fiber material.

BRIEF DESCRIPTION OF THE DRAWINGS

25 The invention is explained in the following description in view of the drawings that show:

FIG. 1 illustrates a gas turbine in accordance with an aspect of the present invention.

30 FIG. 2 illustrates a ceramic matrix composite structure in accordance with an aspect of the present invention.

FIG. 3 illustrates an impregnated fiber material in accordance with an aspect of the present invention.

FIG. 4 illustrates a trimodal distribution of ceramic particles in accordance with an aspect of the present invention.

5 FIG. 5 illustrates a process for forming a ceramic matrix composite structure in accordance with an aspect of the present invention.

FIG. 6 illustrates another process for forming a ceramic matrix composite structure in accordance with an aspect of the present invention.

10 FIG. 7 illustrates an example of a prior art turbine component having interlaminar cracking as a result of such anisotropic shrinkage.

FIG. 8 illustrates an example of a turbine component having optimized in-plane vs. through thickness shrinkage in accordance with an aspect of the present invention.

15 DETAILED DESCRIPTION

Now referring to the figures, FIG. 1 illustrates a gas turbine engine 2 include one or more components formed from a ceramic matrix composite material as described herein. The gas turbine engine 2 includes a compressor section 4, a combustor section 6, and a turbine section 8. In the turbine section 8, there are alternating rows of stationary airfoils 18 (commonly referred to as "vanes") and rotating airfoils 16 (commonly referred to as "blades"). Each row of blades 16 is formed by a circular array of airfoils connected to an attachment disc 14 disposed on a rotor 10 having a rotor axis 12. The blades 16 extend radially outward from the rotor 10 and terminate in blades tips. The vanes 18 extend radially inward from an inner surface of vane carriers 22, 24 which are attached to an outer casing 26 of the engine 2.

Between the rows of vanes 18 a ring seal 20 is attached to the inner surface of the vane carrier 22. The ring seal 20 is a stationary component that acts as a hot gas path guide between the rows of vanes 18 at the locations of the rotating blades 16. The ring seal 20 is commonly formed by a plurality of ring segments (not shown) that are attached either directly to the

vane carriers 22, 24 or indirectly such as by attachment to metal isolation rings (not shown) attached to the vane carriers 22, 24. During engine operation, high-temperature/high-velocity gases 28 flow primarily axially with respect to the rotor axis 12 through the rows of vanes 18 and blades 16 in the turbine section 8.

In accordance with an aspect of the present invention and referring to FIG. 2, there is shown a portion of a ceramic matrix composite (CMC) structure 100 having a composition as described herein. In an embodiment, the CMC structure 100 comprises at least a portion of a component of the gas turbine 2 shown in FIG. 1, such as a portion of a blade 16, vane 18, or ring segment thereof. For example, in an embodiment, the CMC structure (material) 100 may comprise at least an airfoil portion of the blade 16 or vane 18. As shown in FIG. 2, the CMC structure 100 comprises a matrix 102 of a ceramic material (ceramic matrix 104) which is reinforced with a fiber material 106. It is understood that the structure 100 of FIG. 2 represents a fully sintered ceramic matrix composite material, and thus the distinction between the fiber material 106 and the matrix 102 may not be so evident in the actual structure but is differentiated here for ease of illustration.

In the CMC structure 100, the fiber material 106 comprises any suitable material formed from fibers which will provide a degree of reinforcement to the matrix 102. In an embodiment and as shown in FIG. 2, the fiber material 106 comprises a plurality of successive layers of ceramic fibers. For example, in the embodiment shown in FIG. 2, the fiber material 106 comprises a plurality of plies 108 of the fiber material 106. Within each layer, the fibers may be continuous or long discontinuous fibers, and may be oriented in a direction generally parallel, perpendicular, or otherwise disposed relative to a major length of the fiber material 106. In addition, the fibers of each layer may be provided in various forms, such as a woven fabric, blankets, unidirectional tapes, and mats.

Further, the fiber material 106 may be formed from any suitable material such as an oxide or non-oxide material. In an embodiment, the fiber

material 106 comprises an oxide material. Exemplary oxide fiber materials for use herein include Al_2O_3 , $\text{Al}_2\text{O}_3\text{—SiO}_2$, mullite, YAG or $\text{Al}_2\text{O}_3\text{—YAG}$ eutectics, for example. Further exemplary fiber materials are available from the Minnesota Mining and Manufacturing Company (3M) under the trademark NEXTEL, including NEXTEL 720 (alumino-silicate), NEXTEL 610 (alumina) and NEXTEL 650 (alumina and zirconia). The fibers may be wrapped in a dry state or may be pre-impregnated with a matrix precursor (e.g., matrix particles as explained below) such as particles of alumina, mullite, or alumino-silicate, for example.

To provide the ceramic matrix composite structure 100, the fiber material 106 is impregnated or otherwise provided with a medium (e.g., slurry) comprising ceramic or ceramic precursor particles (hereinafter “ceramic particles 110”) (see FIG. 3) to form an impregnated fiber material 107. Following sintering of the impregnated fiber material 107 shown in FIG. 3, the ceramic matrix composite structure 100 is formed (FIG. 2). In certain embodiments, a medium comprising the ceramic particles 110 is pre-impregnated into individual layers of the fiber material 106, and is thus provided in a “pre-preg” form as is known in the art. Thereafter, the individual layers (which may be in a pre-preg form) are stacked on one another to form a desired component thickness and shape, and thereafter are subjected to a heat treatment process, e.g., a sintering protocol, to provide the CMC structure 100.

In other embodiments, individual layers of the fiber material 106 are not pre-impregnated with the ceramic particles 110, but instead a plurality of layers, e.g., plies 108, of the fiber material 106 are stacked on one another in a desired fashion, and then are impregnated with a medium carrying the ceramic particles 110. In any case, during sintering, the ceramic particles melt into the fiber material 106 and the impregnated fiber material 106 is sintered to form the structure 100. Exemplary techniques for introducing the ceramic particles 110 into one or more layers the fiber material 106 include gas deposition, melt infiltration, chemical vapor infiltration, slurry infiltration,

preceramic polymer pyrolysis, chemical reactions, sintering, or electrophoretic deposition of ceramic powders, thereby creating the CMC structure 100 with a fiber reinforced ceramic matrix. Further processes for forming a ceramic matrix composite structure (material) are also described in U.S. Patent Nos. 8,058,191; 7,745,022, 7,153,096; 7,093,359; and 6,733,907, the entirety of each of which is hereby incorporated by reference.

It is appreciated that the ceramic particles 110 may be in any suitable form such as a powder. The powder may comprise any suitable oxide or non-oxide material, such as alumina, mullite, aluminosilicate, yttria alumina garnet, silicon carbide, silicon nitride, silicon carbonitride, and the like, or a precursor thereof. In particular embodiments, the ceramic particles 110 comprise an oxide material. As mentioned, the ceramic particles 110 may be incorporated into the fiber material 106 within a suitable medium for carrying the particles. In some instances, the medium assists in the formation of the desired matrix 102. In an embodiment, for example, the ceramic particles 110 may comprise an oxide (e.g., alumina) powder within a medium, such as tetra-ethyl-orthosilicate (as an Si donor) and aluminum-butylate (as an Al donor). In other embodiments, sol-gel chemistry is utilized to carry the ceramic particles 110 into the fiber material 106.

Whether by pre-preg or following lay up, once the fiber material 106 is laid down in its desired thickness and orientation and includes the ceramic particles 110, the impregnated fiber material 107 is then subjected to a sintering process in order to provide the final ceramic matrix composite structure 100. As is known in the art, the sintering process may be done at a temperature and for a duration effective to ensure flow of the medium comprising the ceramic particles 110 into or about the fiber material 106 and suitable drying to form the desired ceramic matrix composite structure 100. In an embodiment, the sintering is done at a temperature of from 500 to 1300° C, isocratic or with a gradient, for a duration of from 1 to 24 hours.

In accordance with an aspect of the present invention, the present inventors have recognized in conventional processes that the through

thickness shrinkage (shown as arrow 112 in FIG. 3) during sintering is substantially greater than the in plane shrinkage (shown as arrow 114 in FIG. 3). As mentioned, this is due in part to the fact that the fiber material 106 is typically already sintered prior to impregnation with the ceramic particles, and thus is substantially less prone to shrinkage in the in plane direction. When left unaddressed as is conventional, this differential shrinkage or anisotropic sintering shrinkage will lead to defects (e.g., voids and cracks) in the CMC structure 100, and even poorer interlaminar strength of the CMC material upon being subjected to the high temperatures typical of gas turbine operation. As used herein, "in-plane" means parallel to the main plane of the fibers (e.g., parallel to the individual plies 108) of the CMC structure, and "through-plane" or "through thickness" means vertically through the fibers (e.g., vertically through plies 108) or transverse thereto.

Accordingly, aspects of the present invention address anisotropic sintering shrinkage by disclosing processes and structures that utilize ceramic particles 110 of a mixture of sizes (e.g., average diameter size) which substantially reduce anisotropic sintering shrinkage. Referring to FIGS. 2-3 and 5, there is shown a first step of a process 200 for forming a ceramic matrix composite structure 100 and reducing anisotropic shrinkage. The process comprises step 202 of impregnating the fiber material 106 with at least first ceramic particles 116 and second ceramic particles 118 in a suitable medium to form an impregnated fiber material 107. The second particles 118 have a smaller average diameter relative to the first ceramic particles 116. Following impregnation of the first and second ceramic particles 116, 118 into the fiber material 106, the process 200 comprises step 204 of sintering the impregnated fiber material 107 to produce the ceramic matrix composite structure;

In accordance with one aspect, the process 200 utilizes first ceramic particles 116 and second ceramic particles 118 of an average particle size in the impregnating step 202 effective to provide a through thickness shrinkage of 1.0 percent (0.01) or less for the impregnated fiber material 107 during the

sintering step 204. In this way, the size (e.g., average diameter) of the first ceramic particles 116 and the second ceramic particles 118 minimize anisotropic sintering shrinkage of the impregnated fiber material 106 during sintering. In an embodiment of the process 200, the present inventors have found that the anisotropic sintering shrinkage is sufficiently reduced if the through thickness shrinkage is kept below a value of 1.0 % (0.01) or less according to formula (I) below:

$$(I) \quad S = t/R$$

wherein R = the average diameter of the first ceramic particles 116;

wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

In another embodiment, the through thickness shrinkage is 0.5 percent (.005) or less, and in a particular embodiment the through thickness shrinkage is 0.1 percent (.001) or less. The lower the through thickness shrinkage, the more likely the through thickness shrinkage will match the in plane shrinkage, which again is generally expected to be relatively low due to the presence of pre-sintered fibers.

In certain embodiments, at least two of the parameters in formula (I) above are known and at least one parameter is solved for. For example, in an embodiment, the desired through thickness shrinkage is known and the average diameter of the second ceramic particles 118 is known. In this embodiment, the first ceramic particles 116 for the impregnating step have an average diameter according to the formula:

$$(II) \quad R = t/S:$$

wherein R = the average diameter of the first ceramic particles 116;

wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

By way of example, if the desired through thickness shrinkage is 0.5% (or 0.005) and the second ceramic particles 11 have an average diameter of

0.1 micron, the average diameter for the first particles 116 can be selected according to formula (II). In this instance, $R = t/S$ or $0.1/0.005 = 20$ micron. Accordingly, first ceramic particles 116 of an average diameter of 20 micron and second ceramic particles 118 of an average diameter of 0.1 can be
5 utilized to bring about the desired through thickness shrinkage of 0.005 (0.5 percent) or less, thereby reducing anisotropic sintering shrinkage.

In another embodiment, the desired through thickness shrinkage is known and the average diameter of first ceramic particles 116 is known, and the process 200 may thus further comprise utilizing second ceramic particles
10 118 for the impregnating step having an average diameter according to the formula:

$$(III) \quad t = SR:$$

wherein R = the average diameter of the first ceramic particles 116;

wherein S = the through thickness shrinkage of the impregnated fiber

15 material 107; and

wherein t = the average diameter of the second ceramic particles 118.

Thus, by way of example again, if the desired through thickness shrinkage is 0.4 % (.004) or less and the first ceramic particles 116 have an average diameter size of 35 micron, then the second ceramic particles 118
20 may be selected for use in the impregnating step having an average diameter size of $t = 0.004 \times 35 = 0.14$ micron.

In any embodiment described herein, the through thickness shrinkage value (S) may be one which at least a predetermined percentage of a known in plane shrinkage value for the impregnated fiber material 107. In an
25 embodiment, the predetermined percentage is at least (within) 50% of an in plane shrinkage of the impregnated fiber material 107, and in another embodiment at least (within) 75% of the in plane shrinkage, and in a particular embodiment at least (within) 95% of the in plane shrinkage. Thus, "within 50, 75, or 95 percent or the like" as used herein means a through thickness value
30 that is at least 50, 75, 95, or the like of a value for the in plane shrinkage.

It is appreciated that the ceramic particles 110 may comprise two or more distinct average diameter sizes. The above embodiment illustrated ceramic particles 110 as comprising first ceramic particles 116 and second ceramic particles 118 having two distinct average diameter sizes. In accordance with another aspect and as shown in FIG. 4, the ceramic particles 110, however, may comprise three or more particles sizes. For example, FIG. 4 illustrates ceramic particles 110 as comprising first ceramic particles 116, second ceramic particles 118, and third ceramic particles 120, wherein the third ceramic particles 120 have an average diameter that is between that of the first ceramic particles 116 and the second ceramic particles 118.

When the third ceramic particles 120 are present, the third ceramic particles 120 may have an average diameter according to the formula:

$$(IV) \quad t = SR:$$

wherein R = the average diameter of the first ceramic particles 116;

wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the third ceramic particles 120.

Thus, the size of the third ceramic particles 120 can be selected according to the same formula utilized to select the second ceramic particles 118 in order to reduce anisotropic sintering shrinkage during formation of the ceramic matrix composite structure 100.

In accordance with another aspect, there is disclosed another embodiment of a process 300 for forming a ceramic matrix composite structure 100. As shown in FIGS. 2-3 and 6, the process 300 also includes step 302 of impregnating a fiber material 106 comprising a plurality of layers of ceramic fibers with a medium comprising a plurality of ceramic particles 110 to form an impregnated fiber material 107, wherein the particles 110 comprise at least first ceramic particles 116 and second ceramic particles 118. The second ceramic particles 118 have an average diameter which is less than an average diameter of the first ceramic particles 116. In addition, the process

300 includes step 302 of sintering the impregnated fiber material 107 to produce the ceramic matrix composite structure 100.

In the process 300, the average diameter of the first and second ceramic particles 116, 118 for the impregnating step 302 provide a through thickness shrinkage during the sintering which is at least 50% of an in plane shrinkage for the impregnated fiber material 107. In another embodiment, the predetermined percentage is at least 75% of an in plane shrinkage of the impregnated fiber material 107, and in another embodiment at least 95% of the in plane shrinkage.

In an embodiment, in the process 300, the first ceramic particles 116 and second ceramic particles 118 have an average diameter such that they provide a desired through thickness shrinkage (at least 50% of the in plane shrinkage) according to the formula (I) as was described above, wherein:

$$(I) \quad S = t/R$$

wherein R = the average diameter of the first ceramic particles 116; wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

In an embodiment, the through thickness shrinkage is 1.0 percent (.01) or less, and in another embodiment is 0.5 percent (.005) or less, and in a particular embodiment is 0.1 percent (.001) or less.

In an embodiment for the process 300, when two of the three parameters are known (such as the desired through thickness shrinkage and an average diameter of one of the first and second particles), the average diameter of the first ceramic particles 116 and the second ceramic particles 118 can be similarly determined as described above in process 200 according to formulas (II) and (III).

In still other embodiments for the process 300, third ceramic particles 120 may be provided and the third ceramic particles 120 for the impregnating step may have an average diameter according to the formula:

$$(IV) \quad t = SR:$$

wherein R = the average diameter of the first ceramic particles 116;

wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

5 In this way, the size of the third ceramic particles 120 can be selected according to the same formula utilized to select the second ceramic particles 118 in order to reduce anisotropic sintering shrinkage in forming the ceramic matrix composite structure 100.

10 In accordance with an aspect of the present invention, there is provided a ceramic matrix composite structure 100 formed by the processes described herein. Referring again to FIG. 3, the structure 100 comprises an impregnated fiber material 107 comprising a medium (e.g., a slurry) comprising a plurality of ceramic particles 110 impregnated into a fiber material 106 comprising plurality of layers of ceramic fibers. The ceramic
15 particles 110 comprise at least first ceramic particles 116 and second ceramic particles 118. The second ceramic particles comprise an average diameter which is less than an average diameter of the first ceramic particles. In addition, the first ceramic particles 116 and second ceramic particles 118 are effective to provide a through thickness shrinkage which is at least (within)
20 50% of an in plane shrinkage upon sintering of the impregnated fiber material 107. In another embodiment, the through thickness shrinkage is at least (within) 75% of the in plane shrinkage, and in a particular embodiment is at least (within) 95% of the in plane shrinkage.

In one embodiment, the average diameter of the first ceramic particles
25 116 and the second particles 118 provides a through thickness shrinkage for the ceramic matrix composite structure 100 of 1.0 percent (.01) or less upon sintering of the impregnated fiber material 107 according to the formula:

$$(I) \quad S = t/R$$

wherein R = the average diameter of the first ceramic particles 116;

30 wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

In another embodiment, the through thickness shrinkage is 0.5 percent (.005) or less, and in a particular embodiment is 0.1 percent (.001) or less. In addition, in certain embodiments, the average diameter of the first ceramic particles 116 and the second particles 118 may also provide a through thickness shrinkage for the ceramic matrix composite structure 100 that is at least 50% of an in plane shrinkage of the impregnated fiber material 107 upon sintering, the through thickness shrinkage provided according to the formula:

$$(I) \quad S = t/R$$

wherein R = the average diameter of the first ceramic particles 116;
wherein S = the through thickness shrinkage of the impregnated fiber material 107; and

wherein t = the average diameter of the second ceramic particles 118.

In any of the processes 200, 300 and structures 100 described herein, the average diameter of the first ceramic particles 116 utilized in the impregnating step may be from 0.1 to 50 microns, and in a particular embodiment from 0.1 to 20 microns. In addition, the average diameter of the second ceramic particles 118 utilized in the impregnating step may be from 0.01 to 0.2 microns. Further, in certain embodiments and when present, the average diameter of the third ceramic particles 118 utilized in the impregnating step may be from 0.1 to 0.4 microns. As described herein, these values may be determined according to the formulas described herein or selected as a starting point (known value) in the formulas.

In certain embodiments, in any of the processes 200, 300 and structures described herein, the average diameter of the first ceramic particles 116 is such that the first ceramic particles 116 fit in between the various fiber layers constituting the fiber material 106. In addition, in such embodiments, the second ceramic particles 118 (and any additional sized ceramic particles, e.g., third ceramic particles 120) may comprise an average diameter such that these particles (118, 120) infiltrate the fibers of the fiber material 106, and are thus disposed within the fiber material 106. So doing may further reduce the

through thickness shrinkage during sintering of the impregnated fiber material 107.

Further, in any of the processes 200, 300 and structures 100 described herein, a ratio of an average diameter of the first ceramic particles 116 to the second ceramic particles 118 may be provided to optimize packing of the particles 116, 118. So doing may further enhance reduction of the through thickness shrinkage for the ceramic matrix composite structure 100, e.g., by providing a smaller delta through to which the particles may cause shrinkage during sintering. By way of example, the average size of the particles 116, 118 may be such that a second ceramic particle 118 fits within a gap formed by three or more of the first ceramic particles 116. In another aspect, the present inventors have found that a particle size ratio ($R = D_{\text{first}} / D_{\text{second}}$) of an average diameter of the first ceramic particles 116 to an average diameter of the second ceramic particles 118 of at least 7:1 promotes the tight packing of the particles 38 to a packing density of at least 80%. In accordance with an aspect, the particle size ratio is from 7:1 to 10:1.

Further, in any of the processes and structures described herein, the anisotropic sintering shrinkage may be further reduced by optimizing a volume ratio of the first ceramic particles 116 to the second ceramic particles 118 (hereinafter "volume ratio (VR).") In an embodiment, the volume ratio comprises at least 60%, wherein the volume ratio is defined by the formula:

$$(III) \quad \text{Volume ratio (VR)} = \text{Volume}_{\text{first}} / (\text{Volume}_{\text{first}} + \text{Volume}_{\text{second}})$$

In a particular embodiment, the volume ratio is from 70 to 80 %. A volume ratio of 60% or more is believed to provide sufficient first particles 116 to allow for second particles 118 to fit therebetween.

The above-described components and systems describe novel and inventive components and processes for making CMC structures with minimal to no anisotropic sintering strain. In addition, the processes described herein may be utilized to build any suitable CMC structure, including but not limited to any component of the gas turbine engine 2 shown in FIG. 1, including but not limited to blades, vanes, ring segments, or the like. The resulting CMC

structures show markedly improved structural integrity as a result of reduced anisotropic sintering strain as described herein. Contrasted with previous FIG. 7 showing interlaminar cracking as a result of mismatched in plane and through thickness shrinkage, FIG. 8 illustrates an example of a component
5 manufactured according to the processes described herein having a microstructure with more closely matched in-plane and through thickness shrinkage rates as provided by aspects of the present invention. Thus, the manufactured component is not only produced with minimal structural defects at the outset, but is also less prone to cracking over a service life of the
10 component as fewer defects/cracks exist from which propagation may take place.

While various embodiments of the present invention have been shown and described herein, it will be obvious that such embodiments are provided by way of example only. Numerous variations, changes and substitutions
15 may be made without departing from the invention herein. Accordingly, it is intended that the invention be limited only by the spirit and scope of the appended claims.

CLAIMS

What we claim is:

1. A process for making a ceramic matrix composite structure (100)
5 comprising:

impregnating a fiber material (106) comprising a plurality of layers of
ceramic fibers with a medium comprising a plurality of ceramic particles (110)
to form an impregnated fiber material (107), wherein the particles (110)
comprise at least first ceramic particles (116) and second ceramic particles
10 (118), the second ceramic particles (118) having an average diameter less
than an average diameter of the first ceramic particles (116);

sintering the impregnated fiber material (107) to produce the ceramic
matrix composite structure (100);

wherein the process comprises utilizing first ceramic particles (116)
15 and second ceramic particles (118) of an average particle size in the
impregnating step effective to provide a through thickness shrinkage of 1.0
percent or less for the impregnated fiber material (107) during the sintering,
wherein the through thickness shrinkage is determined according to the
formula:

20
$$S = t/R$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber
material (107); and

wherein t = the average diameter of the second ceramic particles (118).

25

2. The process of claim 1, wherein the average diameter of the first
ceramic particles (116) and the second ceramic particles (118) provides a
through thickness shrinkage for the ceramic matrix composite structure (100)
of 0.5 percent or less.

30

3. The process of claim 1, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) provides a through thickness shrinkage for the ceramic matrix composite structure (100) of 0.1 percent or less.

5

4. The process of claim 1, wherein the through thickness shrinkage and the average diameter of second ceramic particles (118) are known, and wherein the first ceramic particles (116) utilized in the impregnating step have an average diameter according to the formula:

10

$$R = t/S:$$

wherein R = the average diameter of the first ceramic particles (116);
wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

wherein t = the average diameter of the second ceramic particles (118).

15

5. The process of claim 1, wherein the through thickness shrinkage and the average diameter of first ceramic particles (116) are known, and wherein the second ceramic particles (118) utilized in the impregnating step have an average diameter according to the formula:

20

$$t = SR:$$

wherein R = the average diameter of the first ceramic particles (116);
wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

wherein t = the average diameter of the second ceramic particles (118).

25

6. The process of claim 1, wherein the ceramic particles (110) further comprise third ceramic particles (120 having an average diameter between that of the first ceramic particles (116) and the second ceramic particles (118), and wherein the third ceramic particles (120) utilized in the
5 impregnating step have an average diameter according to the formula:

$$t = SR:$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

10 wherein t = the average diameter of the third ceramic particles (120).

7. The process of claim 1, wherein the average diameter of the first ceramic particles (116) is from 0.1 to 50 microns.

15 8. The process of claim 1, wherein the average diameter of the second ceramic particles (118) is from 0.01 to 0.2 microns.

9. The process of claim 1, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) provides a
20 through thickness shrinkage during the sintering which is at least 50% of an in plane shrinkage for the ceramic matrix composite structure (100).

10. The process of claim 1, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) provides a
25 through thickness shrinkage during the sintering which is at least 75% of an in plane shrinkage for the ceramic matrix composite structure (100).

11. The process of claim 1, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) is a through thickness shrinkage during the sintering which is at least 95% of an in plane shrinkage for the ceramic matrix composite structure (100).

5

12. The process of claim 1, wherein the first ceramic particles (116) are disposed between adjacent layers of the fiber material (106) and the second ceramic particles (118) are infiltrated within the fiber material (106).

10

13. The process of claim 1, wherein a particle size ratio (R) of an average diameter of the first ceramic particles (116) to an average diameter of the second ceramic particles (118) is at least 7:1 according to the formula: $R = D_{\text{first}} / D_{\text{second}}$.

15

14. The process of claim 13, wherein the particle size ratio is from 7:1 to 10:1.

20

15. The process of claim 1, wherein a volume ratio of the first ceramic particles (116) to the second ceramic particles (118) is at least 60%, and wherein the volume ratio is defined by the formula $(VR) = \text{Volume}_{\text{first}} / (\text{Volume}_{\text{coarse}} + \text{Volume}_{\text{fine}})$.

25

30

16. A process for making a ceramic matrix composite structure comprising:

impregnating a fiber material (106) comprising a plurality of layers of ceramic fibers with a medium comprising a plurality of ceramic particles (110) to form an impregnated fiber material (107), wherein the particles (110) comprise at least first ceramic particles (116) and second ceramic particles (118), the second ceramic particles (118) having an average diameter less than an average diameter of the first ceramic particles (116); and

sintering the impregnated fiber material (107) to produce the ceramic matrix composite structure (100);

wherein the average diameters of the first ceramic particles (116) and the second ceramic particles (118) provide a through thickness shrinkage during the sintering which is at least 50% of an in plane shrinkage for the impregnated fiber material (107) upon sintering.

17. The process of claim 16, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) provide a through thickness shrinkage during the sintering which is at least 75% of an in plane shrinkage for the ceramic matrix composite structure (100).

18. The process of claim 16, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) provide a through thickness shrinkage during the sintering which is at least 95% of an in plane shrinkage for the ceramic matrix composite structure (100).

19. The process of claim 16, wherein the process comprises utilizing first ceramic particles (116) and second ceramic particles (118) of an average particle size in the impregnating step effective to provide a through thickness shrinkage of 1.0 percent or less for the impregnated fiber material (107)

5 during the sintering, wherein the through thickness shrinkage is determined according to the formula:

$$S = t/R$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber

10 material (107); and

wherein t = the average diameter of the second ceramic particles (118).

20. The process of claim 16, wherein the average diameters of the first ceramic particles (116) and the second ceramic particles (118) provide a
15 through thickness shrinkage for the ceramic matrix composite structure (100) of 0.5 percent or less.

21. The process of claim 16, wherein the average diameters of the first ceramic particles (116) and the second ceramic particles (118) provide a
20 through thickness shrinkage for the ceramic matrix composite structure (100) of 0.1 percent or less.

22. The process of claim 16, wherein the process comprises utilizing first ceramic particles (116) and second ceramic particles (118) of an average particle size in the impregnating step effective to provide a through thickness shrinkage of 1.0 percent or less for the impregnated fiber material (107) during the sintering, wherein the through thickness shrinkage is determined according to the formula:

$$S = t/R$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber

10 material (107); and

wherein t = the average diameter of the second ceramic particles (118).

23. The process of claim 22, wherein the through thickness shrinkage and the average diameter of second ceramic particles (118) are known, and wherein the process further comprises first ceramic particles (116) have an average diameter for the impregnating step according to the formula:

$$R = t/S:$$

wherein R = the average diameter of the first ceramic particles (116);

20 wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

wherein t = the average diameter of the second ceramic particles (118).

24. The process of claim 22, wherein the through thickness shrinkage and the average diameter of first ceramic particles (116) is known, and wherein the second ceramic particles (118) have an average particle size for the impregnating step according to the formula:

5
$$t = SR:$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

wherein t = the average diameter of the second ceramic particles (118).

10

25. The process of claim 22, wherein the ceramic particles (110) further comprise third ceramic particles (120) having an average diameter between that of the first ceramic particles (116) and the second ceramic particles (118), and wherein the method further comprises utilizing the third ceramic particles (120) in the impregnating step having an average diameter according to the formula:

15

$$t = SR:$$

wherein R = the average diameter of the first ceramic particles (116);

wherein S = the through thickness shrinkage of the impregnated fiber

20 material (107); and

wherein t = the average diameter of the third ceramic particles (120).

26. The process of claim 16, wherein the average diameter of the first ceramic particles (116) is from 0.1 to 50 microns.

25

27. The process of claim 16, wherein the average diameter of the second ceramic particles (118) is from 0.01 to 0.2 microns.

30

28. The process of claim 16, wherein the first ceramic particles (116) are disposed between adjacent layers of the fiber material (106) and the second ceramic particles (118) are infiltrated within the fiber material (106).

5 29. The process of claim 16, wherein a particle size ratio (R) of an average diameter of the first ceramic particles (116) to an average diameter of the second ceramic particles (118) is at least 7:1 according to the formula: $R = D_{\text{first}} / D_{\text{second}}$.

10 30. The process of claim 29, wherein the particle size ratio is from 7:1 to 10:1.

31. The process of claim 16, wherein a volume ratio of the first ceramic particles (116) to the second ceramic particles (118) is at least 60%,
15 and wherein the volume ratio is defined by the formula $(VR) = \text{Volume}_{\text{first}} / (\text{Volume}_{\text{coarse}} + V_{\text{fine}})$.

32. A ceramic matrix composite structure (100) comprising:
a fiber material (106) comprising plurality of layers of ceramic fibers;
20 an impregnated fiber material (107) comprising a fiber material (106) impregnated with a medium comprising a plurality of ceramic particles (110);
wherein the ceramic particles (100) comprise at least first ceramic particles (116) and second ceramic particles (118), the second ceramic particles (118) having an average diameter less than an average diameter of
25 the first ceramic particles (116); and

wherein an average diameter of the first ceramic particles (116) and the second ceramic particles (118) is effective to provide a through thickness shrinkage which is at least 50% of an in plane shrinkage for the impregnated fiber material (107) upon sintering of the impregnated fiber material (107).

33. The ceramic matrix composite structure (100) of claim 32, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) is effective to provide a through thickness shrinkage upon sintering which is at least 75% of an in plane shrinkage for the ceramic matrix composite structure (100).

34. The process of claim 32, wherein the average diameter of the first ceramic particles (116) and the second ceramic particles (118) is effective to provide a through thickness shrinkage upon sintering which is within 95% of an in plane shrinkage for the ceramic matrix composite structure (100).

35. The ceramic matrix composite structure (100) of claim 32, wherein the average diameter of the first ceramic particles (116) and second ceramic particles (118) are effective to provide a through thickness shrinkage of 1.0 percent or less for the impregnated fiber material (107) upon sintering, wherein the through thickness shrinkage is determined according to the formula:

$$S = t/R$$

wherein R = the average diameter of the first ceramic particles (116);
wherein S = the through thickness shrinkage of the impregnated fiber material (107); and

wherein t = the average diameter of the second ceramic particles (118).

36. The ceramic matrix composite structure (100) of claim 32, wherein the ceramic particles (110) further comprise third ceramic particles (120 having an average diameter between that of the first ceramic particles (116) and the second ceramic particles (118).

37. The ceramic matrix composite structure (100) of claim 32, wherein the average diameter of the first ceramic particles (116) is from 0.1 to 50 microns.

38. The ceramic matrix composite structure (100) of claim 32, wherein the average diameter of the second ceramic particles (118) is from 0.01 to 0.2 microns.

5

39. The ceramic matrix composite structure (100) of claim 32, wherein the first ceramic particles (116) are disposed between adjacent layers of the fiber material (106) and the second ceramic particles (118) are infiltrated within the fiber material (106).

10

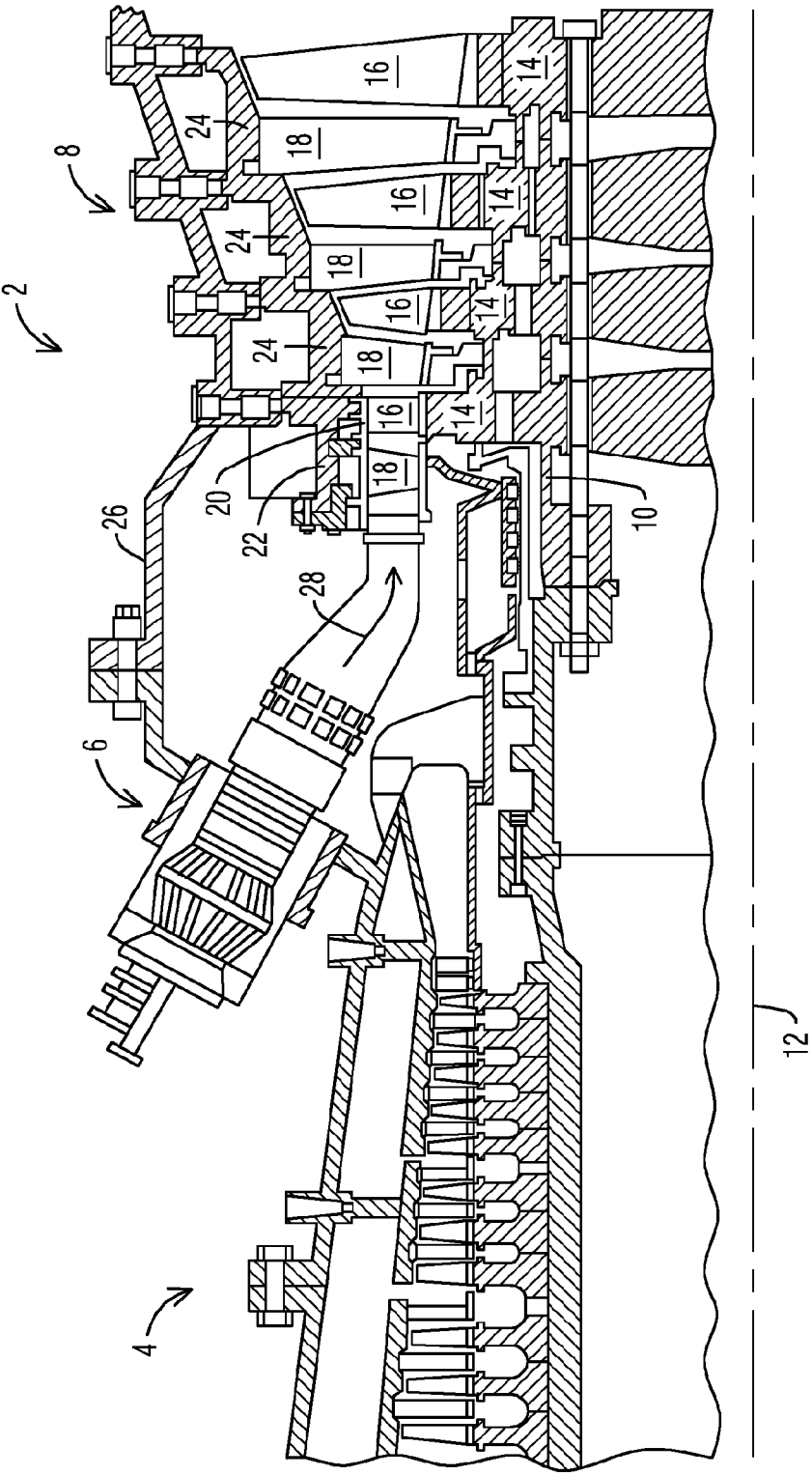
40. The ceramic matrix composite structure (100) of claim 32, wherein a particle size ratio (R) of an average diameter of the first ceramic particles (116) to an average diameter of the second ceramic particles (118) is at least 7:1 according to the formula: $R = D_{\text{first}} / D_{\text{second}}$.

15

41. The ceramic matrix composite structure (100) of claim 32, wherein a volume ratio of the first ceramic particles (116) to the second ceramic particles (118) is at least 60%, and wherein the volume ratio is defined by the formula $(VR) = \text{Volume}_{\text{first}} / (\text{Volume}_{\text{coarse}} + \text{Volume}_{\text{fine}})$.

20

FIG. 1



2/3

FIG. 2

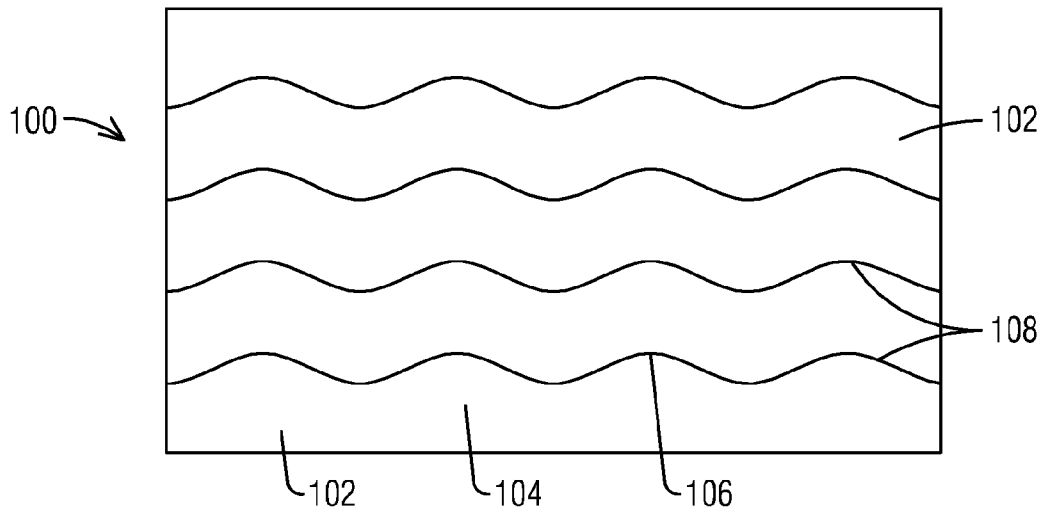


FIG. 3

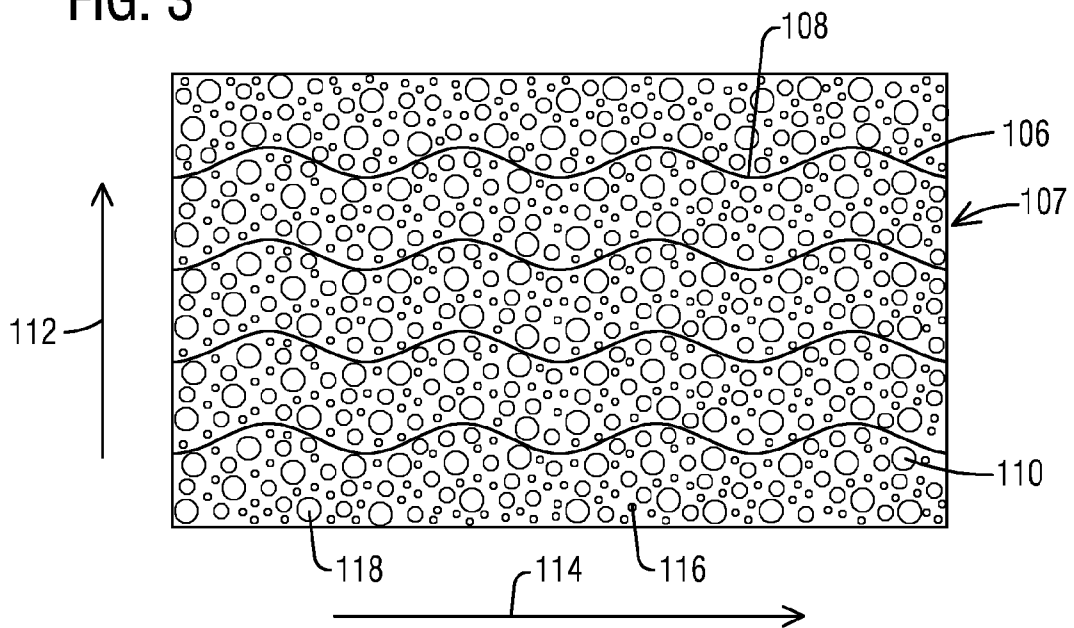
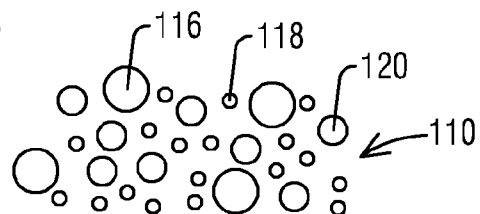


FIG. 4



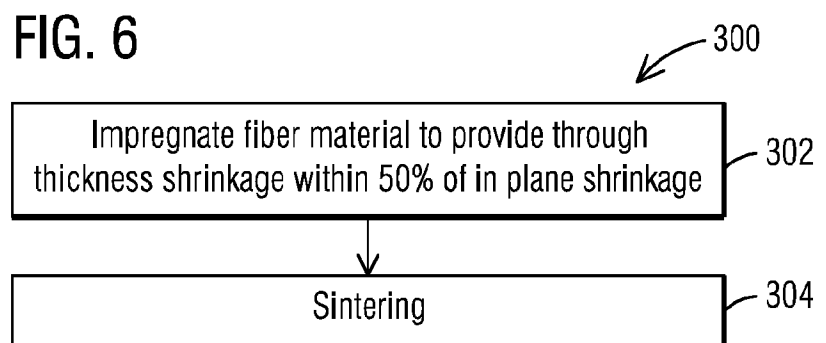
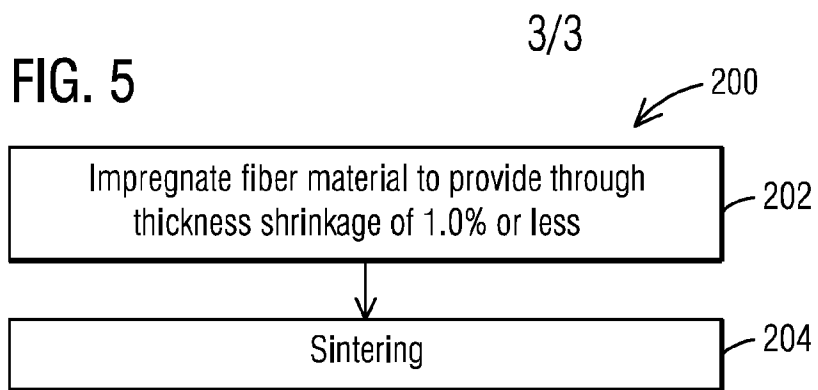


FIG. 7

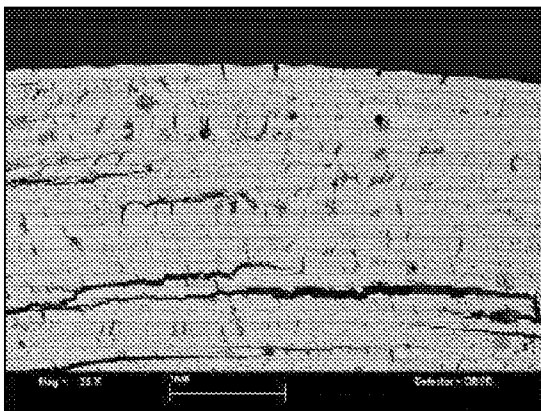
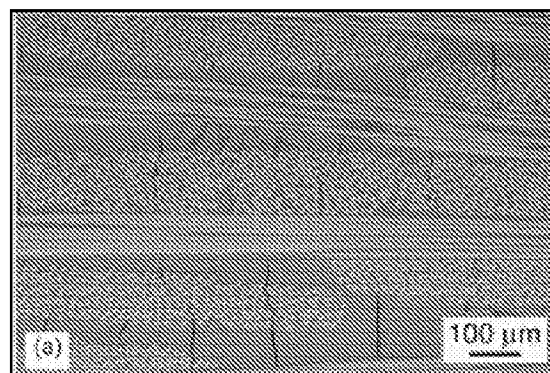


FIG. 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/043476

A. CLASSIFICATION OF SUBJECT MATTER INV. B32B18/00 C04B35/117 C04B35/18 C04B35/185 C04B35/626 C04B35/80 ADD. 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) B32B 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 practicable, search terms used) EPO-Internal, WPI Data, INSPEC, COMPENDEX											
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="vertical-align: top;">X A</td> <td style="vertical-align: top;"> US 2017/313627 A1 (SHIM SUNGBO [US] ET AL) 2 November 2017 (2017-11-02) paragraph [0019]; claims 1-7 </td> <td style="vertical-align: top;"> 1,4-19, 22-41 2,3,20, 21 </td> </tr> <tr> <td style="vertical-align: top;">X A</td> <td style="vertical-align: top;"> ----- WO 2012/084917 A1 (EADS DEUTSCHLAND GMBH [DE]; WILHELMI CHRISTIAN [DE]; MACHRY THAYS [DE]) 28 June 2012 (2012-06-28) page 12, line 19 - page 14, line 25 page 36, line 5 - line 7 page 38, line 16 - line 24 ----- </td> <td style="vertical-align: top;"> 1,2, 4-20, 22-41 3,21 </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X A	US 2017/313627 A1 (SHIM SUNGBO [US] ET AL) 2 November 2017 (2017-11-02) paragraph [0019]; claims 1-7	1,4-19, 22-41 2,3,20, 21	X A	----- WO 2012/084917 A1 (EADS DEUTSCHLAND GMBH [DE]; WILHELMI CHRISTIAN [DE]; MACHRY THAYS [DE]) 28 June 2012 (2012-06-28) page 12, line 19 - page 14, line 25 page 36, line 5 - line 7 page 38, line 16 - line 24 -----	1,2, 4-20, 22-41 3,21
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
X A	US 2017/313627 A1 (SHIM SUNGBO [US] ET AL) 2 November 2017 (2017-11-02) paragraph [0019]; claims 1-7	1,4-19, 22-41 2,3,20, 21									
X A	----- WO 2012/084917 A1 (EADS DEUTSCHLAND GMBH [DE]; WILHELMI CHRISTIAN [DE]; MACHRY THAYS [DE]) 28 June 2012 (2012-06-28) page 12, line 19 - page 14, line 25 page 36, line 5 - line 7 page 38, line 16 - line 24 -----	1,2, 4-20, 22-41 3,21									
☐ Further documents are listed in the continuation of Box C. ☒ See patent family 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 application or patent 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 20 March 2019		Date of mailing of the international search report 29/03/2019									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Raming, Tomas									

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/043476

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017313627 A1	02-11-2017	EP 3241815 A1	08-11-2017
		US 2017313627 A1	02-11-2017

WO 2012084917 A1	28-06-2012	DE 102010055221 A1	21-06-2012
		EP 2661344 A1	13-11-2013
		ES 2651117 T3	24-01-2018
		WO 2012084917 A1	28-06-2012
