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(54) Title: MULTI-LAYER FIBER COATING CONTAINING A SIC AND BN COATING LAYER

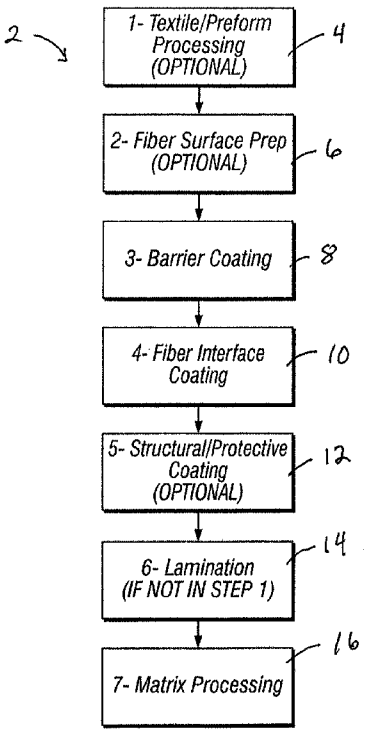


FIG. 1

(57) Abstract: A multi-layer fiber coating is provided which, in an illustrative embodiment, includes: a ceramic grade Nicalon preform; a silicon carbide coat applied over the fibers; a boron nitride interface coat applied over the silicon carbide coat; wherein the boron nitride coat has a thickness of about 0.5 micron; a silicon carbide coat applied over the boron nitride coat; and wherein the silicon carbide has a thickness of about 2 micron. A multi-layer fiber coating, comprising: a Tyranno Lox-M fiber coated in tow form with 1 micron of silicon carbide by a chemical vapor deposition process and about 1 micron of silicon nitride; a silicon doped boron nitride coat is applied over the about 1 micron of silicon nitride; and wherein the doped boron nitride coat has a thickness of 0.3 micron is also provided. A multi-layer fiber coating, comprising: a T-300 carbon fiber preform; a coat that is graded from PyC to SiC is applied over the T-300 carbon fiber preform; wherein the graded PyC to SiC coat has a thickness of about 1.5 micron; a silicon doped boron nitride interface coat is applied over the graded PyC to SiC coat; wherein the silicon doped boron nitride interface coat has a thickness of about 0.5 micron; and a silicon carbide coat of 2 micron is applied over the silicon doped boron nitride interface coat, is also provided.

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MULTI-LAYER FIBER COATING CONTAINING A SIC AND BN COATING LAYER

RELATED APPLICATIONS

[0001] This application is related to and claims priority to U.S. Provisional Patent Application Serial No. 61/783,845 filed on March 14, 2013 entitled "Multi-Layer Fiber Coating." The subject matter disclosed in that provisional application is hereby expressly incorporated into the present application in its entirety.

FIELD OF THE DISCLOSURE

[0002] The present disclosure relates to multi-layer fiber coatings, and particularly to multi-layer fiber coatings for ceramic fiber applications.

BACKGROUND

[0003] Economical and environmental concerns, i.e. improving efficiency and reducing emissions, are driving forces behind the ever increasing demand for higher gas turbine inlet temperatures. A limitation to the efficiency and emissions of many gas turbine engines is the temperature capability of hot section components such as blades, vanes, blade tracks, and combustor liners. Technology improvements in cooling, materials, and coatings are required to achieve higher inlet temperatures. As the temperature capability of Ni-based superalloys has approached their intrinsic limit, further improvements in their temperature capability have become increasingly difficult. Therefore, the emphasis in gas turbine materials development has shifted to thermal barrier coatings (TBC) and next generation high temperature materials, such as ceramic-based materials.

[0004] Silicon Carbide/Silicon Carbide (SiC/SiC) Ceramic Material Composite (CMC) materials are prime candidates to replace Ni-based superalloys for hot section structural components for next generation gas turbine engines. The key benefit of SiC/SiC CMC engine components is their excellent high temperature mechanical, physical, and chemical properties which allow gas turbine engines to operate at much higher temperatures than the current engines

having superalloy components. SiC/SiC CMCs also provide the additional benefit of damage tolerance, which monolithic ceramics do not possess.

SUMMARY

[0005] The present disclosure includes a multi-layer fiber coatings for ceramic fiber applications.

[0006] An illustrative embodiment of the present disclosure provides a multi-layer fiber coating which comprises: a ceramic grade Nicalon preform; a silicon carbide coat applied over the fibers; wherein the silicon carbide coat has a thickness of about 1 µm; a boron nitride interface coat applied over the silicon carbide coat; wherein the boron nitride coat has a thickness of about 0.5 µm; a silicon carbide coat applied over the boron nitride coat; and wherein the silicon carbide has a thickness of about 2 µm.

[0007] In the above and other embodiments, the multi-layer fiber coating may further comprise: the Nicalon preform including about 36% fiber volume; the Nicalon preform being assembled in a tooling for chemical vapor infiltration; the silicon carbide coat having an effective fiber volume of about 39%; the Nicalon preform being cleaned using air at about 600 degrees C to remove sizing char; the preform being completed with slurry and melt infiltration; the 1 µm of silicon carbide being applied by chemical vapor infiltration; the 2 µm of silicon carbide being applied by chemical vapor infiltration.

[0008] Another illustrative embodiment of the present disclosure provides a multi-layer fiber coating which comprises: a Tyranno Lox-M fiber coated in tow form with 1 µm of silicon carbide by a chemical vapor deposition process and about 1 µm of silicon nitride; a silicon doped boron nitride coat is applied over the about 1 µm of silicon nitride; and wherein the doped boron nitride coat has a thickness of 0.3 µm.

[0009] In the above and other embodiments, the multi-layer fiber coating may further comprise: the Tyranno Lox-M fiber in the tow being coated with silicon nitride of about 0.3 µm and silicon carbide of about 0.1 µm; the tow being processed with a silicon carbide slurry and binders to form a uni-directional tape;

the tapes being laminated and shaped, then cured; and a resulting body that is infiltrated with silicon to complete the CMC component.

[0010] Another illustrative embodiment of the present disclosure provides a multi-layer fiber coating which comprises: a T-300 carbon fiber preform; a coat that is graded from PyC to SiC is applied over the T-300 carbon fiber preform; wherein the graded PyC to SiC coat has a thickness of about 1.5 µm; a silicon doped boron nitride interface coat is applied over the graded PyC to SiC coat; wherein the silicon doped boron nitride interface coat has a thickness of about 0.5 µm; and a silicon carbide coat of 2 µm is applied over the silicon doped boron nitride interface coat.

[0011] In the above and other embodiments, the multi-layer fiber coating may further comprise: the T-300 carbon fiber preform includes about 36% fiber volume; the T-300 carbon fiber preform is assembled in tooling for chemical vapor infiltration; a silicon nitride coat of about 0.2 µm being applied over the silicon carbide coat; the graded PyC to SiC coat being applied by chemical vapor infiltration; the silicon carbide coating of 2 µm being applied by chemical vapor infiltration; and the silicon nitride coat of 0.2 µm being applied by chemical vapor infiltration.

[0012] It should be appreciated that the present application discloses one or more of the features recited in the appended claims and/or the following features which alone or in any combination may comprise patentable subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Fig. 1 is a flow diagram showing a multi-layer process according to the present disclosure; and

[0014] Fig. 2 is an end view of ceramic fibers showing an “improved” multi-layer coating.

DETAILED DESCRIPTION

[0015] The present disclosure includes a fiber coating that incorporates at least one layer prior to the fiber interface coating to improve chemical

compatibility of the fiber and interface coating. Illustratively, the first coating is bonded to the fiber and is followed by an interface coating and optionally additional coatings. The coating may be a slightly altered composition of the fiber or a totally different composition. The coating acts as barrier between incompatible elements.

[0016] The coating may also "heal" surface flaws on the fiber and to increase the effective fiber volume by increasing the diameter of the fiber. The coating may be uniform in composition and structure, graded intentionally to produce a better match between the fiber and the interface coating or consist of multiple thin layers prior to the interface coating. The coating may be followed by other functional coatings prior to the interface coating to improve structural performance or environmental resistance.

[0017] The coating may range from 0.01 μm to 2 μm, and may be deposited by chemical vapor deposition, physical vapor deposition (including directed vapor deposition) or other suitable means. The fiber in the composite may be carbon, ceramic (silicon carbide, alumina, aluminosilicate, SiNC etc.) or glass. The coating (or coating layers) may consist of elemental, binary or ternary compounds of the following elements: carbon, nitrogen, oxygen, silicon, germanium, boron, aluminum, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, nickel, scandium, yttrium, ytterbium and rhenium.

[0018] Illustratively, it may be desirable to tailor the coating composition and/or structure to produce a slightly lower modulus than the fiber to reduce stress in the coating layer and delay surface cracking.

[0019] A flow diagram depicting a process 2 of applying a barrier coating on a fiber is shown in Fig. 1. The first step of process 2 is providing the fiber material, textile, or preform, for processing at 4. Illustratively, the fiber surface may be prepared by cleaning it using high temperature air to remove sizing char at 6. A barrier coating is then applied over the fiber at 8. This barrier coating may be a silicon carbide coating applied by chemical vapor infiltration, for example. Over the barrier coating, the fiber interface coating is supplied at 10.

Such an interface coating may include boron nitride. A structural and protective coating 12 may be applied over interface coating 10. The structural coating may be silicon carbide applied by chemical vapor infiltration. Optionally, additional fiber layers may be applied at 14 after the structural coating if not already done in step 1 of process 2. Lastly, a CMC matrix may be completed with slurry and melt infiltration at 16.

[0020] An end sectional view of fiber material 18 is shown in Fig. 2. A barrier coating 20 such as that described with respect to step 8 in Fig. 1 is applied over top of fiber 18. An interface coating 22 is applied over the barrier coating. Lastly, the structural protective layer coating 24 is applied on top pursuant step 12 of process 2.

[0021] Advantages of this multi-layer coating may include: enabling use of lower cost fibers with oxygen sensitive interface coatings like boron nitride; reducing or eliminating damage to fiber surfaces during interface coating deposition (e.g. incompatibility of carbon and BN deposition); the additional layer providing an opportunity to manage thermal and mechanical incompatibilities between a fiber an subsequent coatings and additional oxidation resistance to the fiber; increasing ultimate strength resulting from surface defect reduction; and increasing creep strength if the fiber coating has higher creep capability than the fiber.

[0022] The following are non-limiting illustrative embodiments of a barrier coating:

[0023] **Preform Based CMC**

[0024] 1. A ceramic grade Nicalon preform constructed of 36% fiber volume and assembled in tooling for chemical vapor infiltration (CVI);

[0025] 2. the preform is cleaned using air at 600 degrees C to remove sizing char from the fiber;

[0026] 3. the fiber is coated with 1 µm of silicon carbide (SiC) by CV, the effective fiber volume is now close to 39%;

[0027] 4. a boron nitride (BN) interface coating is then applied at 0.5 µm;

[0028] 5. a SiC coating of 2 µm is applied by CVI; and

[0029] 6. the CMC matrix is completed with slurry and melt infiltration.

[0030] It is notable that the interface coating remains functional as a result of limited, if any, interaction with oxygen in the fiber.

[0031] **CMC Made with Pre-Coated Fiber**

[0032] 1. Tyranno Lox-M fiber is coated in tow form with 1 µm of SiC by a chemical vapor deposition (CVD) process, and 1µm of silicon nitride;

[0033] 2. a subsequent process applies a silicon doped boron nitride coating of 0.3 µm;

[0034] 3. the fiber in the tow is coated with silicon nitride of 0.3 µm and silicon carbide of 0.1 µm;

[0035] 4. the tow is processed with a SiC slurry and binders to form a tape;

[0036] 5. the tapes are laminated and shaped then cured; and

[0037] 6. the resulting body is infiltrated with silicon to complete the CMC component.

[0038] Again, the interface coating remains functional as a result of limited if any interaction with oxygen in the fiber.

[0039] **Preform Based CMC II**

[0040] 1. A T-300 carbon fiber preform is constructed of 36% fiber volume and assembled in tooling for CVI;

[0041] 2. the fiber is coated with a layer that is graded from PyC to SiC over 1.5 µm by CVI;

[0042] 3. a silicon doped boron nitride (BN) interface coating of 0.5 µm is applied;

[0043] 4. a SiC coating of 2 µm is then applied by CVI; [correct?]

[0044] 5. a silicon nitride coating of 0.2 µm is applied by CVI; and

[0045] 6. the CMC matrix is completed through slurry and melt infiltration.

[0046] The resulting composite has an interface coating with improved oxidation resistance compared to the typical PyC coating and the fiber remains undamaged from the BN deposition process.

[0047] While the disclosure has been described in this detailed description, the same is to be considered as exemplary and not restrictive in character, it being understood that only illustrative embodiments thereof have been described and that changes and modifications that come within the spirit of the disclosure are desired to be protected.

What is claimed is:

1. A multi-layer fiber coating, comprising:
a ceramic grade Nicalon preform;
a silicon carbide coat applied over the fibers;
wherein the silicon carbide coat has a thickness of about 1 µm;
a boron nitride interface coat applied over the silicon carbide coat;
wherein the boron nitride coat has a thickness of about 0.5 µm;
a silicon carbide coat applied over the boron nitride coat; and
wherein the silicon carbide has a thickness of about 2 µm.

2. The multi-layer fiber coating of Claim 1, wherein the Nicalon preform includes about 36% fiber volume.

3. The multi-layer fiber coating of Claim 2, wherein the Nicalon preform is assembled in a tooling for chemical vapor infiltration.

4. The multi-layer fiber coating of Claim 1, wherein the silicon carbide coat has an effective fiber volume of about 39%.

5. The multi-layer fiber coating of Claim 2, wherein the Nicalon preform is cleaned using air at about 600 degrees C to remove sizing char.

6. The multi-layer fiber coating of Claim 1, wherein the preform is completed with slurry and melt infiltration.

7. The multi-layer fiber coating of Claim 1, wherein the 1 µm of silicon carbide is applied by chemical vapor infiltration.

8. The multi-layer fiber coating of Claim 1, wherein the 2 µm of silicon carbide is applied by chemical vapor infiltration.

9. A multi-layer fiber coating, comprising:

a Tyranno Lox-M fiber coated in tow form with 1 µm of silicon carbide by a chemical vapor deposition process and about 1 µm of silicon nitride;

a silicon doped boron nitride coat is applied over the about 1 µm of silicon nitride; and

wherein the doped boron nitride coat has a thickness of 0.3 µm.

10. The multi-layer fiber coating of Claim 9, wherein the Tyranno Lox-M fiber in the tow is coated with silicon nitride of about 0.3 µm and silicon carbide of about 0.1 µm.

11. The multi-layer fiber coating of Claim 9, wherein the tow is processed with a silicon carbide slurry and binders to form a uni-directional tape.

12. The multi-layer fiber coating of Claim 9, wherein the tapes are laminated and shaped, then cured.

13. The multi-layer fiber coating of Claim 9, wherein a resulting body is infiltrated with silicon to complete the CMC component .

14. A multi-layer fiber coating, comprising:

a T-300 carbon fiber preform;

a coat that is graded from PyC to SiC is applied over the T-300 carbon fiber preform;

wherein the graded PyC to SiC coat has a thickness of about 1.5 µm;

a silicon doped boron nitride interface coat is applied over the graded PyC to SiC coat;

wherein the silicon doped boron nitride interface coat has a thickness of about 0.5 µm; and

a silicon carbide coat of 2 µm is applied over the silicon doped boron nitride interface coat.

15. The multi-layer fiber coating of Claim 14, wherein the T-300 carbon fiber preform includes about 36% fiber volume.

16. The multi-layer fiber coating of Claim 14, wherein the T-300 carbon fiber preform is assembled in tooling for chemical vapor infiltration.

17. The multi-layer fiber coating of Claim 14, further comprising a silicon nitride coat of about 0.2 µm is applied over the silicon carbide coat.

18. The multi-layer fiber coating of Claim 14, wherein the graded PyC to SiC coat is applied by chemical vapor infiltration.

19. The multi-layer fiber coating of Claim 14, wherein the silicon carbide coating of 2 µm is applied by chemical vapor infiltration.

20. The multi-layer fiber coating of Claim 14, wherein the silicon nitride coat of 0.2 µm is applied by chemical vapor infiltration.

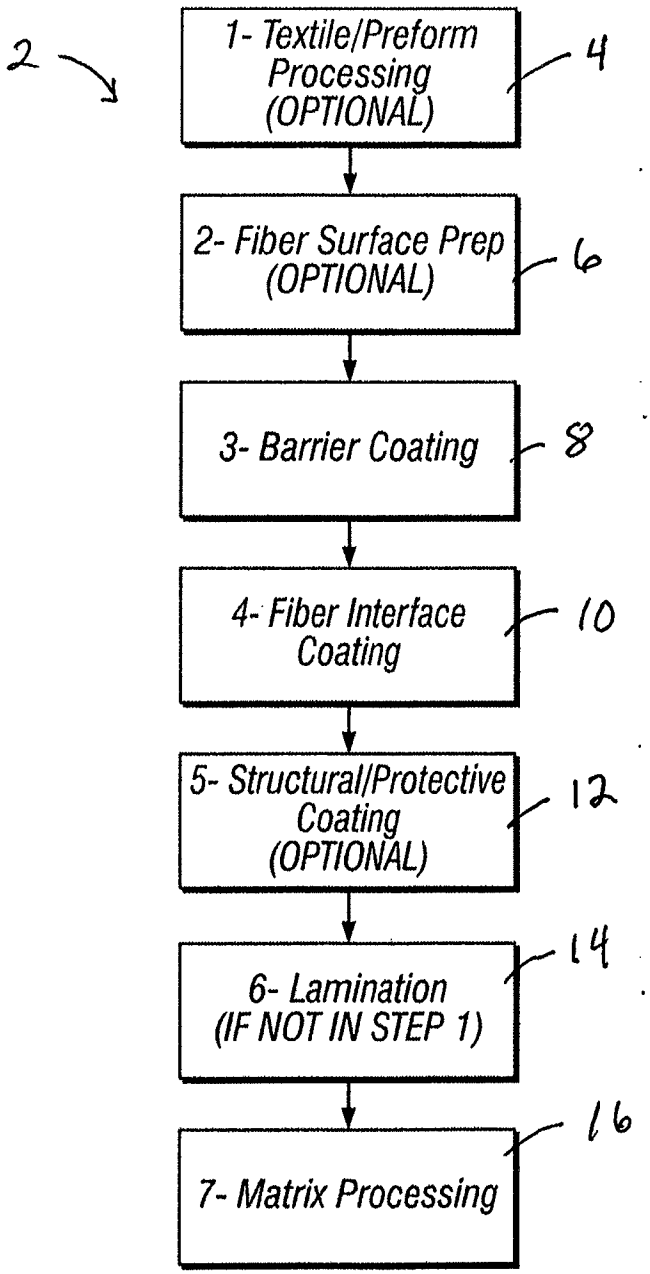

2
1- Textile/Preform Processing (OPTIONAL)
4
2- Fiber Surface Prep (OPTIONAL)
6
3- Barrier Coating
8
4- Fiber Interface Coating
10
5- Structural/Protective Coating (OPTIONAL)
12
6- Lamination (IF NOT IN STEP 1)
14
7- Matrix Processing
16

FIG. 1

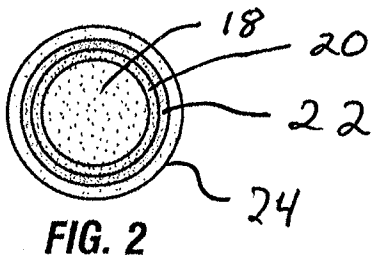

18
20
22
24

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/024175

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B35/565 C04B35/628 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)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 228 453 B1 (FAREED ALI SYED [US] ET AL) 8 May 2001 (2001-05-08)	1-5,7,8
Y	example 10; table VI	6,14-20

Y	US 5 952 100 A (CORMAN GREGORY SCOT [US] ET AL) 14 September 1999 (1999-09-14) example 1	9-13

Y	US 6 024 898 A (STEIBEL JAMES D [US] ET AL) 15 February 2000 (2000-02-15)	6
A	examples A,B,C	1-5,7-20

Y	US 2002/019306 A1 (PETRAK DANIEL RALPH [US]) 14 February 2002 (2002-02-14) example 3	9-13

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/024175

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 939 216 A (KAMEDA TSUNEJI [JP] ET AL) 17 August 1999 (1999-08-17) examples 1,6	1-13
A	US 2006/147688 A1 (SUBRAMANIAN SURESH [US] ET AL) 6 July 2006 (2006-07-06) claim 8	9-13
Y	US 2012/164430 A1 (THEBAULT JACQUES [FR] ET AL) 28 June 2012 (2012-06-28) claim 1; examples 1-5	14-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/024175

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6228453 B1	08-05-2001	AU 741440 B2	29-11-2001
		AU 2084999 A	17-05-1999
		CA 2307854 A1	06-05-1999
		DE 69830510 D1	14-07-2005
		DE 69830510 T2	23-03-2006
		EP 1028926 A2	23-08-2000
		JP 2001520973 A	06-11-2001
		US 6228453 B1	08-05-2001
		US 2002058107 A1	16-05-2002
		WO 9921805 A2	06-05-1999
US 5952100 A	14-09-1999	TW 522089 B	01-03-2003
		US 5952100 A	14-09-1999
		US 6365233 B1	02-04-2002
US 6024898 A	15-02-2000	US 6024898 A	15-02-2000
		US 6258737 B1	10-07-2001
US 2002019306 A1	14-02-2002	DE 69909714 D1	28-08-2003
		DE 69909714 T2	15-04-2004
		EP 1004559 A2	31-05-2000
		JP 4727781 B2	20-07-2011
		JP 2000169249 A	20-06-2000
		US 2002019306 A1	14-02-2002
		US 2002079623 A1	27-06-2002
US 5939216 A	17-08-1999	DE 69607056 D1	20-04-2000
		DE 69607056 T2	09-11-2000
		EP 0742185 A1	13-11-1996
		US 5939216 A	17-08-1999
US 2006147688 A1	06-07-2006	US 2006147688 A1	06-07-2006
		US 2009317612 A1	24-12-2009
US 2012164430 A1	28-06-2012	CA 2774231 A1	31-03-2011
		CN 102470630 A	23-05-2012
		EP 2483073 A1	08-08-2012
		FR 2950622 A1	01-04-2011
		JP 2013505857 A	21-02-2013
		KR 20120079834 A	13-07-2012
		RU 2012114237 A	10-11-2013
		US 2012164430 A1	28-06-2012
		WO 2011036358 A1	31-03-2011