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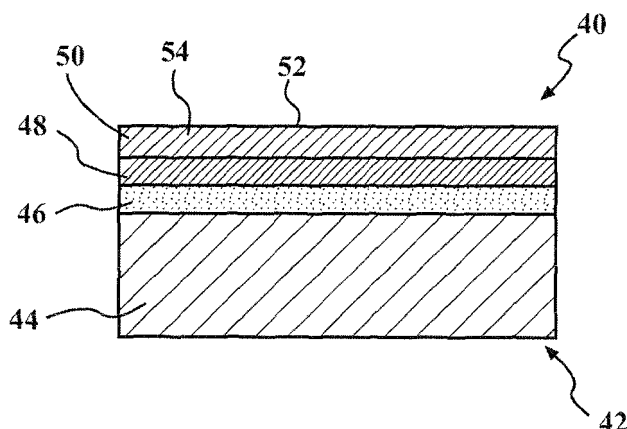
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(54) **CALCIUM MAGNESIUM ALUMINOSILICATE (CMAS) RESISTANT THERMAL BARRIER COATING AND COATING PROCESS THEREFOR**

(57) A process for coating a component and a coating system including a bond coat (46) on a superalloy substrate (44). A thermal barrier material (48) may be applied to the bond coat and a rare earth apatite (54) may be applied to the thermal barrier material (48) via one of

Suspension Plasma Spray (SPS) and Solution Precursor Plasma Spray (SPPS) to form an exposed surface. The rare earth apatite (54) may be formed as $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which $-2 < y < 2$ and $-2 < x < 2$.

FIG. 3



Description

BACKGROUND

[0001] The present disclosure relates to thermal barrier coating compositions designed to withstand infiltration from molten environmental contaminant infiltration, processes for applying same and components coated with same.

[0002] Gas turbine engines typically include a compressor to pressurize airflow, a combustor to burn a hydrocarbon fuel in the presence of the pressurized air, and a turbine to extract energy from the resultant combustion gases. The combustor and the turbine form a hot section of the engine and components therein often include thermal barrier coatings (TBC).

[0003] The thermal insulation provided by the TBC enables hot section components to survive higher operating temperatures, increases component durability, and improves engine durability. The TBC is typically a refractory ceramic material deposited on a bond coat to form what may be termed a TBC system. Bond coat materials widely used in TBC systems include oxidation-resistant overlay coatings such as MCrAlX (where M is iron, cobalt and/or nickel, and X is yttrium or another rare earth element), and diffusion coatings such as diffusion aluminides that contain aluminum intermetallics.

[0004] Ceramic materials and particularly binary yttria-stabilized zirconia (YSZ) are widely used as TBC materials because of their high temperature capability, low thermal conductivity, and relative ease of deposition such as by air plasma spraying (APS), flame spraying such as high-velocity oxy-fuel (HVOF), physical vapor deposition (PVD) and other techniques.

[0005] Under service conditions, these TBC coated hot section engine components can be susceptible to various modes of damage, including erosion, oxidation and corrosion from exposure to the gaseous products of combustion, foreign object damage and attack from environmental contaminants. These contaminants, CMAS (Calcium Magnesium Aluminosilicate), Volcanic Ash, Fly Ash, can adhere to the TBC surfaces of the hot section components. The interaction between the TBC and contaminants may result in premature TBC loss over the life of the components. For example, CMAS particulates are often contained in the atmosphere of areas having fine sand and/or dust. CMAS infiltration is a phenomenon that is linked to TBC spallation. The CMAS may melt on the hot section components, which may lead to penetration of the porous, and strain tolerant, TBC microstructure. On cooling, this penetrated layer stiffens and the induced strain energy can lead to TBC spallation.

[0006] Rare earth zirconates are often utilized to react with the encroaching CMAS melt which may decrease the depth of infiltration of the melt and hence the strain energy introduced into the coating to prevent extensive coating spallation. However, formation of this reaction layer is not readily controllable in service, as a number

of extrinsic factors such as CMAS deposition rate, surface temperatures, airflow, erosion of the TBC, and foreign object damage may result in variation in penetration depth and the potential resultant damage.

SUMMARY

[0007] A process for coating a component according to one disclosed non-limiting embodiment of the present disclosure includes applying a bond coat on a substrate of a component; applying a thermal barrier material to said bond coat; and applying a rare earth apatite to said thermal barrier material.

[0008] A further embodiment of the present disclosure includes, forming said rare earth apatite as a layer with a thickness of about 0.05-20 mil (0.00127-0.508 mm).

[0009] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said rare earth apatite is formed as $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which $-2 < y < 2$ and $-2 < x < 2$.

[0010] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein $0 < y < 2$ and $-2 < x < 0$.

[0011] A further embodiment of any of the foregoing embodiments of the present disclosure includes, where-as applying said rare earth apatite is formed via one of Suspension Plasma Spray (SPS) and Solution Precursor Plasma Spray (SPPS) to form an exposed surface.

[0012] A further embodiment of any of the foregoing embodiments of the present disclosure includes, applying a layer of rare earth zirconate onto said thermal barrier material prior to application of said rare earth apatite.

[0013] A further embodiment of any of the foregoing embodiments of the present disclosure includes, said layer of rare earth zirconate is formed as a layer with a thickness of about 1-20 mil (0.0254 - 0.508 mm).

[0014] A further embodiment of any of the foregoing embodiments of the present disclosure includes, mixing said rare earth apatite and said rare earth zirconate forming a randomly dispersed system.

[0015] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said randomly dispersed system forms a ratio between 80% - 20% rare earth apatite.

[0016] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said randomly dispersed system forms a ratio between 60% - 40% rare earth apatite.

[0017] A further embodiment of any of the foregoing embodiments of the present disclosure includes, mixing said rare earth apatite and said rare earth zirconate forming a graded layer.

[0018] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said graded layer is deposited as 100% rare earth zirconate at said thermal barrier material and gradually transition to 100% rare earth apatite at said exposed surface.

[0019] A gas turbine engine component according to another disclosed non-limiting embodiment of the present disclosure includes a superalloy substrate; a bond coat on said substrate; a thermal barrier material on said bond coat; and a rare earth apatite on said thermal barrier material, said rare earth apatite is formed as a $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which $-2 < y < 2$ and $-2 < x < 2$.

[0020] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein the $0 < y < 2$ and $-2 < x < 0$.

[0021] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said rare earth apatite is formed as a layer with a thickness of about 0.05-20 mil (0.00127-0.508 mm).

[0022] A further embodiment of any of the foregoing embodiments of the present disclosure includes, a layer of rare earth zirconate between said thermal barrier material and said rare earth apatite.

[0023] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said layer of rare earth zirconate is formed as a layer with a thickness of about 1-20 mil (0.0254 - 0.508 mm).

[0024] A further embodiment of any of the foregoing embodiments of the present disclosure includes, a rare earth zirconate mixed with said rare earth apatite to form a randomly dispersed system.

[0025] A further embodiment of any of the foregoing embodiments of the present disclosure includes, a rare earth zirconate mixed with said rare earth apatite to form a graded layer.

[0026] A further embodiment of any of the foregoing embodiments of the present disclosure includes, wherein said rare earth apatite is applied via one of Suspension Plasma Spray (SPS) and Solution Precursor Plasma Spray (SPPS).

[0027] The foregoing features and elements may be combined in various combinations without exclusivity, unless expressly indicated otherwise. These features and elements as well as the operation thereof will become more apparent in light of the following description and the accompanying drawings. It should be understood, however, the following description and drawings are intended to be exemplary in nature and non-limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] Various features will become apparent to those skilled in the art from the following detailed description of the disclosed non-limiting embodiment. The drawings that accompany the detailed description can be briefly described as follows:

Figure 1 is a schematic cross-section of an example gas turbine engine architecture;
Figure 2 is a flowchart of a process according to one disclosed non-limiting embodiment for application of a coating system to a component;

Figure 3 is a cross-section through the coating system applied by the process in accordance with the process of Figure 2;

Figure 4 is a cross-section through a coating system according to another disclosed non-limiting embodiment;

Figure 5 is a flowchart of a process according to another disclosed non-limiting embodiment for the coating system of Figure 4;

Figure 6 is a cross-section through a coating system according to another disclosed non-limiting embodiment;

Figure 7 is a cross-section through a non-homogeneous rare earth apatite layer according to one disclosed non-limiting embodiment;

Figure 8 is a cross-section through a non-homogeneous rare earth apatite layer according to another disclosed non-limiting embodiment;

Figure 9 is a cross-section through a coating system according to another disclosed non-limiting embodiment; and

Figure 10 is a cross-section through a coating system according to another disclosed non-limiting embodiment.

DETAILED DESCRIPTION

[0029] Figure 1 schematically illustrates a gas turbine engine 20. The gas turbine engine 20 is disclosed herein as a two-spool turbo fan that generally incorporates a fan section 22, a compressor section 24, a combustor section 26 and a turbine section 28. The fan section 22 drives air along a bypass flowpath while the compressor section 24 drives air along a core flowpath for compression and communication into the combustor section 26 then expansion through the turbine section 28. Although depicted as a turbofan in the disclosed non-limiting embodiment, it should be understood that the concepts described herein are not limited to use with turbofans as the teachings may be applied to other types of turbomachinery to include, but not be limited to, low bypass augmented turbofans, turbojets, turboshafts, three-spool (plus fan) turbofans and industrial gas turbines.

[0030] With reference to Figure 2, a process 100 according to one disclosed non-limiting embodiment for application of a coating system 40 to a component 42 (Figure 3) subjected to high temperatures is schematically represented. The steps of the process 100 are schematically disclosed in terms of functional block diagrams as a flowchart. It should be appreciated that alternative of addition steps may be provided without departing from the teaching herein.

[0031] Representative examples of the component 42 include but are not limited to combustor section 26 and/or turbine section 28 hardware such as augmentor components, combustor liners, blades, vanes, and blade outer air seals. The coating system 40 as described herein is suitable for protection of a substrate 44 such as a super-

alloy but while being described with reference to such superalloy gas turbine engine components, the teachings herein are generally applicable to any component on which a TBC may be used to protect the component from a high temperature environment, particularly environments containing CMAS.

[0032] The process 100 initially includes application of a bond coat 46 on the substrate 44 (step 102 and Figure 3). The bond coat 46 may include an aluminum-rich composition, such as an overlay coating or a diffusion coating such as a diffusion aluminide or a diffusion platinum aluminide according to formulas such as $M\text{CrAlY}$, $M\text{CrAlY} + \text{Hf}$, and $M\text{CrAlY} + \text{Hf} + \text{Si}$, in which M denotes nickel, cobalt, iron, platinum or mixtures thereof; Cr denotes chromium; Al denotes aluminum; and Y denotes yttrium. $M\text{CrAlY}$ materials are often referred to as overlay coatings because they are applied in a predetermined composition and do not interact significantly with the substrate 44 during the deposition process. One example preferred $M\text{CrAlY}$ bond coat composition has a weight percent compositional range of 5-40 Cr, 8-35 Al, 0.1-2.0 Y, 0.1-7 Si, 0.1-2.0 Hf, balance selected from the group consisting of Ni, Co and mixtures thereof. Alternatively or in addition the bond coat material may include Al, PtAl and the like, that are often referred to as diffusion coatings. Alternatively or in addition, the bond coat material may also include Al, PtAl, $M\text{CrAlY}$ as described above, and the like, that are often referred to as cathodic arc coatings.

[0033] The bond coat 46 may be applied by any method operable to produce a dense, uniform, adherent coating of the desired composition, such as, but not limited to, an overlay bond coat, diffusion bond coat, cathodic arc bond coat, etc. Such techniques may include, but are not limited to, diffusion processes (e.g., inward, outward, etc.), low pressure plasma-spray, air plasma-spray, sputtering, cathodic arc, electron beam physical vapor deposition, high velocity plasma spray techniques (e.g., HVOF, HVAF), combustion processes, wire spray techniques, laser beam cladding, electron beam cladding, etc.

[0034] The particle size for the bond coat 46 may be of any suitable size, and it may be between about 15 microns (0.015 mm) and about 60 microns (0.060 mm) with a mean particle size of about 25 microns (0.025 mm). The bond coat 46 may be applied to any suitable thickness, and may be about 5 mils (0.127 mm) to about 10 mils (0.254 mm) thick. In some embodiments, the thickness may be about 6 mils (0.152 mm) to about 7 mils (0.178 mm) thick.

[0035] Next, a thermal barrier material 48 (Figure 3) may be applied to the bond coat 46 (step 104). The thermal barrier material 48 may include a ceramic based compound. Representative thermal barrier materials include, but are not limited to, a stabilized zirconate, a stabilized hafnate, combinations including at least one of the foregoing compounds, and the like, for example, yttria stabilized zirconia, calcia stabilized zirconia, magnesia

stabilized zirconia, yttria stabilized hafnia, calcia stabilized hafnia and magnesia stabilized hafnia. Yttria stabilized zirconia is commercially available as 7YSZ. One example preferred thermal barrier material 48 is a zirconia stabilized by between 6-8wt% yttria that is about 0.05-5 mil (0.00127 - 0.127 mm) in thickness deposited, nominally at 1-3 mil (0.0254- 0.0761 mm).

[0036] The thermal barrier material 48 may be applied by various known methods. Suitable application methods include, but are not limited to, physical vapor deposition (e.g., electron beam), thermal spray (e.g., air plasma, high velocity oxygen fuel), sputtering, sol gel, slurry, combinations comprising at least one of the foregoing application processes, and the like.

[0037] Next, a Rare Earth Oxide (REO) coat 50 is applied to the thermal barrier material 48 to form the exposed surface 52 (step 106; Figure 2). In this disclosed non-limiting embodiment, the REO coat 50 includes a layer of rare earth apatite 54 that is about 0.05-20 mil (0.00127-0.508 mm) in thickness. The layer of rare earth apatite 54 in this disclosed non-limiting embodiment is a chemically homogenous layer of a distinct composition. The composition of the layer of rare earth apatite 54, for example, may be $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which y and x may range respectively from $-2 < y < 2$ and $-2 < x < 2$, with a preferred range of $0 < y < 2$ and $-2 < x < 0$. It should be appreciated that x and y depend on one another according to a relationship that may change with the stoichiometry, for example, where $x \leq 0$, $y = -x$.

[0038] The layer of rare earth apatite 54 in this disclosed non-limiting embodiment is deposited as densely as possible. Density as defined herein is the ratio of the ceramic material to pores, or open space, within the layer of rare earth apatite 54. For example, an 80% density represents that the layer of rare earth apatite 54 is of 80% ceramic and 20% is of open porosity. In one disclosed non-limiting embodiment, the density ranges from 50-100%, with a preferred range of 80-100%.

[0039] The deposition methodology for the REO coat 50 includes Suspension Plasma Spray (SPS) or Solution Precursor Plasma Spray (SPPS) which facilitate a wide range of chemistries and microstructures to simultaneously optimize cost and strain tolerance. SPS is a form of plasma spraying where the ceramic feedstock is dispersed in a liquid suspension before being injected into the plasma jet which facilitates deposition of finer microstructures through the use of finer powders. SPPS is a solution based process by which a solution of soluble metal cations is injected into a plasma plume. For SPS, the source material for the REO coat 50 may be provided as sub-micron particles dispersed in alcohol, water, or another suitable carrier. For SPPS the source material for the REO coat 50 may be provided as metal salts or metal-organic compounds that would be dispersed in alcohol, water, or other suitable carrier, i.e., Calcium Nitrate + Tetra-ethyl-ortho-silicate + rare earth nitrate in an alcohol solution.

[0040] With reference to Figure 4, in another process

200 according to a disclosed non-limiting embodiment, the process 200 initially includes application of the bond coat 46 then the thermal barrier material 48 (steps 202, 204). The REO coat 50 in this disclosed non-limiting embodiment includes a layer of rare earth zirconate 56 (Figure 5; step 206) of about 1-20 mil (0.0254 - 0.508 mm) thickness between the layer of rare earth apatite 54 and the thermal barrier material 48. That is, the layer of rare earth zirconate 56 is applied to the thermal barrier material 48 then the rare earth apatite 54 is applied to the rare earth zirconate 56. The layer of rare earth zirconate 56 may be a fluorite or pyrochlore and may also be applied via, SPS or SPPS. Example rare earth zirconates include, but are not limited to, yttrium zirconate, neodymium zirconate, gadolinium zirconate, lanthanide series zirconates such as those from elements #57 (La) through #71 (Lu), and mixtures thereof.

[0041] With reference to Figure 6, in another disclosed non-limiting embodiment, the REO coat 50 is non-homogenous. In one disclosed non-limiting embodiment, the non-homogenous REO coat 50 is formed as a graded layer 58 (Figure 7). In one example, the graded layer 58 is deposited as 100% rare earth zirconate 54 and gradually transitions to 100% rare earth apatite 54 over a predetermined distance or number of layers. The desired gradient is readily deposited via SPS or SPPS. It should be appreciated that various gradients may be provided.

[0042] In another disclosed non-limiting embodiment, the non-homogenous REO coat 50 is formed as a randomly dispersed system layer 60 (Figure 8). The randomly dispersed system layer 60 is readily deposited via SPS or SPPS. In one example, a randomly dispersed system includes rare earth zirconate 56 and rare earth apatite 54 in a ratio between 80% - 20% rare earth apatite 54, with a preferred ratio of 60-40%. By providing pre-reacted powder dispersed within the stabilized zirconia, there will be a suitable amount of rare earth apatite 54 that will begin to form a barrier layer while reducing the increases in thermal conductivity that a fully dense homogenous layer (Figure 3) would otherwise provide.

[0043] With reference to Figure 9, in another disclosed non-limiting embodiment, the REO coat 50 includes a layer of rare earth zirconate 56 of about 1-20 mil (0.0254 - 0.508 mm) thick between the thermal barrier material 48 and the non-homogenous REO coat 50. That is, this embodiment is similar to the Figure 4 embodiment but with the top layer being a non-homogenous layer such as in Figures 7 or 8.

[0044] With reference to Figure 10, in another disclosed non-limiting embodiment, the REO coat 50 includes multiple additional alternating layers of rare earth zirconate 56 and non-homogenous rare earth apatite 54. It should be appreciated that various numbers of layers may be provided. Further, one or more graded layers 58 may be graded or a randomly dispersed system.

[0045] The use of SPS and SPPS as a deposition methodology for the REO coat 50 facilitates a wide range of chemistries and microstructures to simultaneously op-

timize cost and strain tolerance.

[0046] The use of the terms "a" and "an" and "the" and similar references in the context of description (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or specifically contradicted by context. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity). All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. It should be appreciated that relative positional terms such as "forward," "aft," "upper," "lower," "above," "below," and the like are with reference to the normal operational attitude of the vehicle and should not be considered otherwise limiting.

[0047] Although the different non-limiting embodiments have specific illustrated components, the embodiments of this invention are not limited to those particular combinations. It is possible to use some of the components or features from any of the non-limiting embodiments in combination with features or components from any of the other non-limiting embodiments.

[0048] It should be appreciated that like reference numerals identify corresponding or similar elements throughout the several drawings. It should also be appreciated that although a particular component arrangement is disclosed in the illustrated embodiment, other arrangements will benefit herefrom.

[0049] Although particular step sequences are shown, described, and claimed, it should be understood that steps may be performed in any order, separated or combined unless otherwise indicated and will still benefit from the present disclosure.

[0050] The foregoing description is exemplary rather than defined by the limitations within. Various non-limiting embodiments are disclosed herein, however, one of ordinary skill in the art would recognize that various modifications and variations in light of the above teachings will fall within the scope of the appended claims. It is therefore to be understood that within the scope of the appended claims, the disclosure may be practiced other than as specifically described. For that reason the appended claims should be studied to determine true scope and content.

Claims

1. A process for coating a component, comprising:

applying a bond coat (46) on a substrate (44) of an component;
applying a thermal barrier material (48) to said bond coat (46); and
applying a rare earth apatite (54) to said thermal barrier material (46).

2. The process as recited in claim 1, wherein said rare earth apatite (54) is formed as $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which $-2 < y < 2$ and $-2 < x < 2$.
3. A gas turbine engine component, comprising:
 - a superalloy substrate (44);
 - a bond coat (46) on said substrate (44);
 - a thermal barrier material (48) on said bond coat (46); and
 - a rare earth apatite (54) on said thermal barrier material (48), said rare earth apatite (54) is formed as a $\text{Ca}_{2+y}\text{RE}_{8+x}(\text{SiO}_4)_6\text{O}_{2+3x/2+y}$ in which $-2 < y < 2$ and $-2 < x < 2$.
4. The process or component as recited in claim 2 or 3, wherein the $0 < y < 2$ and $-2 < x < 0$.
5. The process or component as recited in any preceding claim, wherein said rare earth apatite (54) is formed as a layer with a thickness of about 0.05-20 mil (0.00127-0.508 mm).
6. The process or component as recited in any preceding claim, further comprising (applying) a layer of rare earth zirconate (56) between said thermal barrier material (48) and said rare earth apatite (54).
7. The process or component as recited in claim 6, wherein said layer of rare earth zirconate (56) is formed as a layer with a thickness of about 1-20 mil (0.0254 - 0.508 mm).
8. The process as recited in any of claims 1, 2 or 4 to 7, further comprising mixing said rare earth apatite (54) and a rare earth zirconate forming a randomly dispersed system.
9. The component as recited in any of claims 3 to 7, further comprising a rare earth zirconate (56) mixed with said rare earth apatite (54) to form a randomly dispersed system.
10. The process or component as recited in claim 8 or 9, wherein said randomly dispersed system forms a ratio between 80% - 20% rare earth apatite.
11. The process or component as recited in claim 8 or 9, wherein said randomly dispersed system forms a ratio between 60% - 40% rare earth apatite.
12. The process as recited in any of claims 1, 2 or 4 to 7, further comprising mixing said rare earth apatite (54) and a rare earth zirconate forming a graded layer (58).
13. The component as recited in any of claims 3 to 7, further comprising a rare earth zirconate (56) mixed with said rare earth apatite (54) to form a graded layer (58).
14. The process or component as recited in claim 12 or 13, wherein said graded layer (58) is deposited as 100% rare earth zirconate at said thermal barrier material (48) and gradually transition to 100% rare earth apatite at an exposed surface.
15. The process or component as recited in any preceding claim, wherein said rare earth apatite (54) is applied via one of Suspension Plasma Spray (SPS) and Solution Precursor Plasma Spray (SPPS).

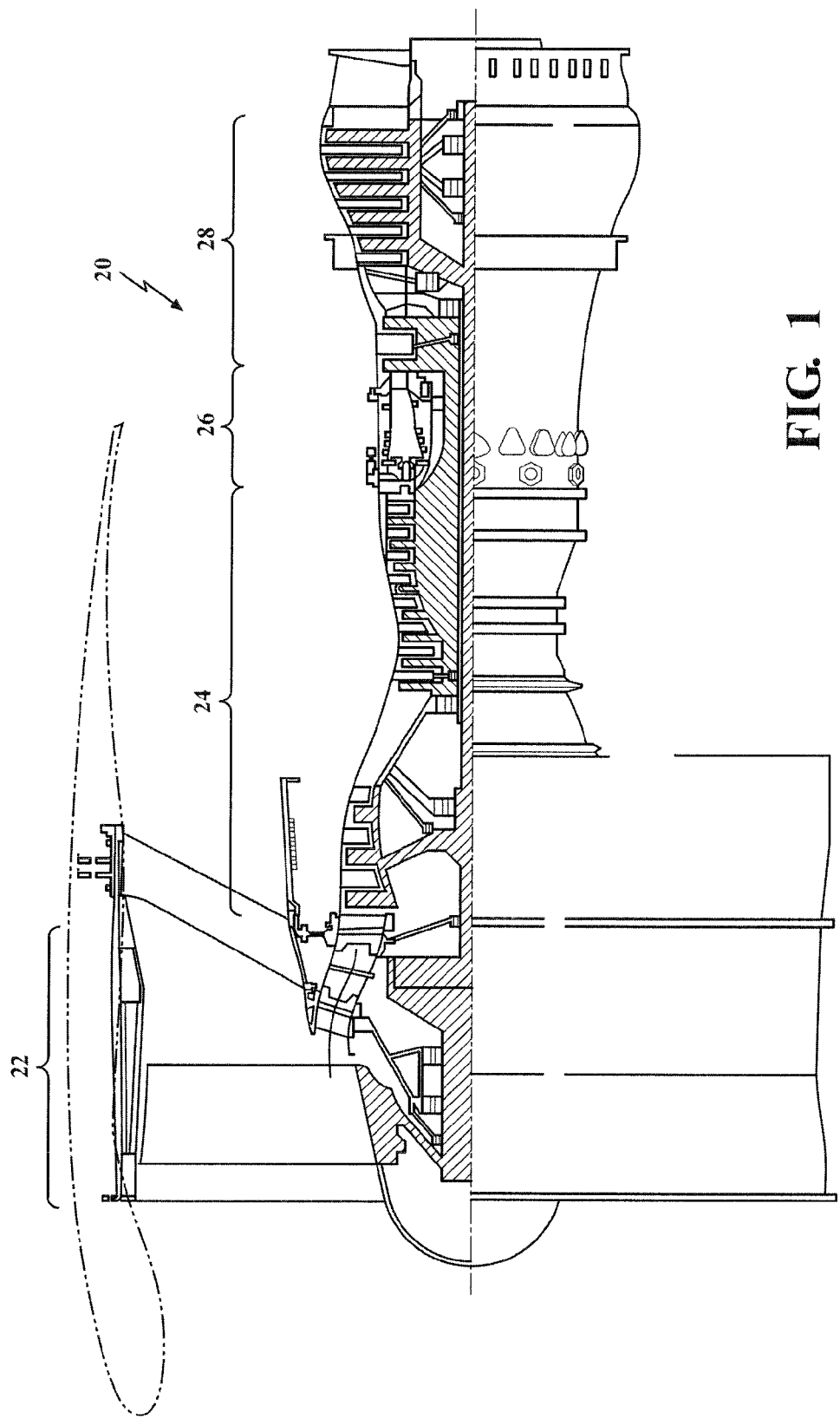


FIG. 1

FIG. 2

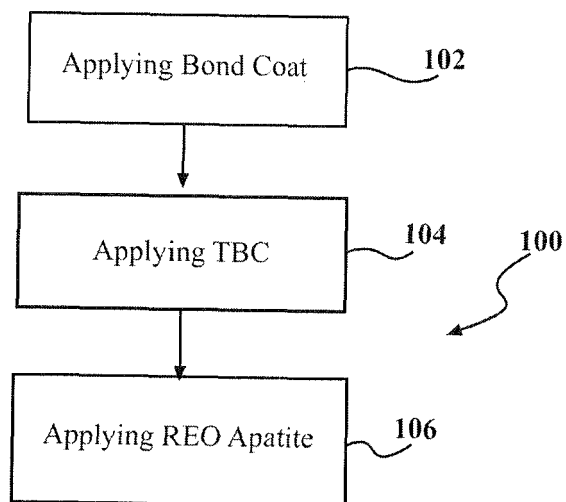


FIG. 3

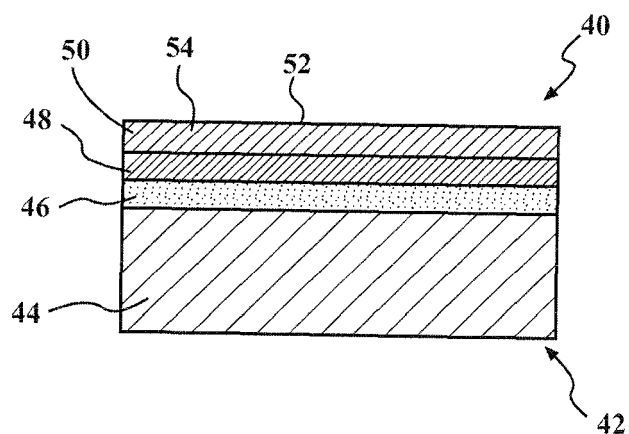


FIG. 4

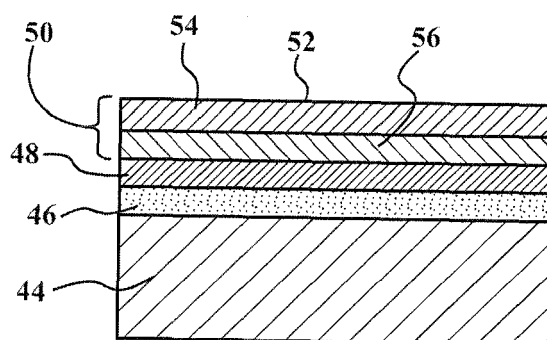


FIG. 5

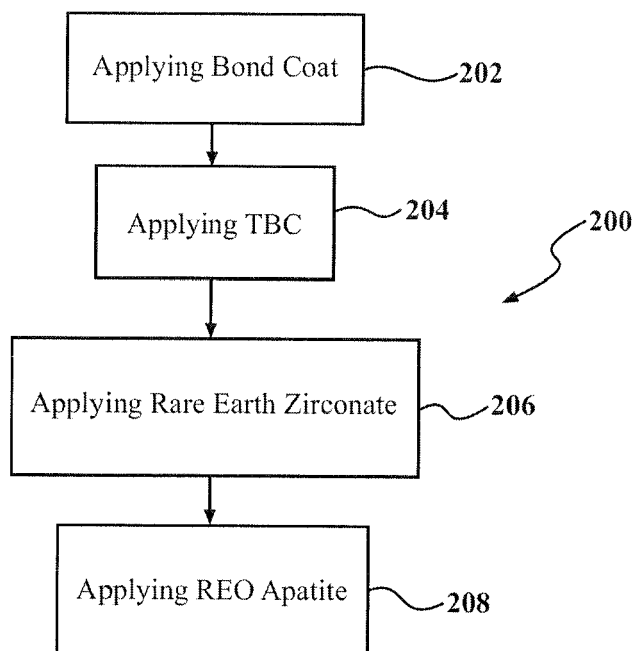


FIG. 6

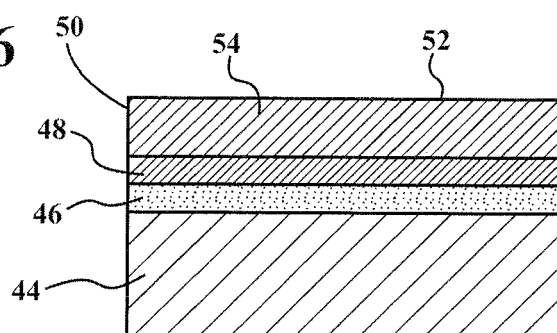


FIG. 7

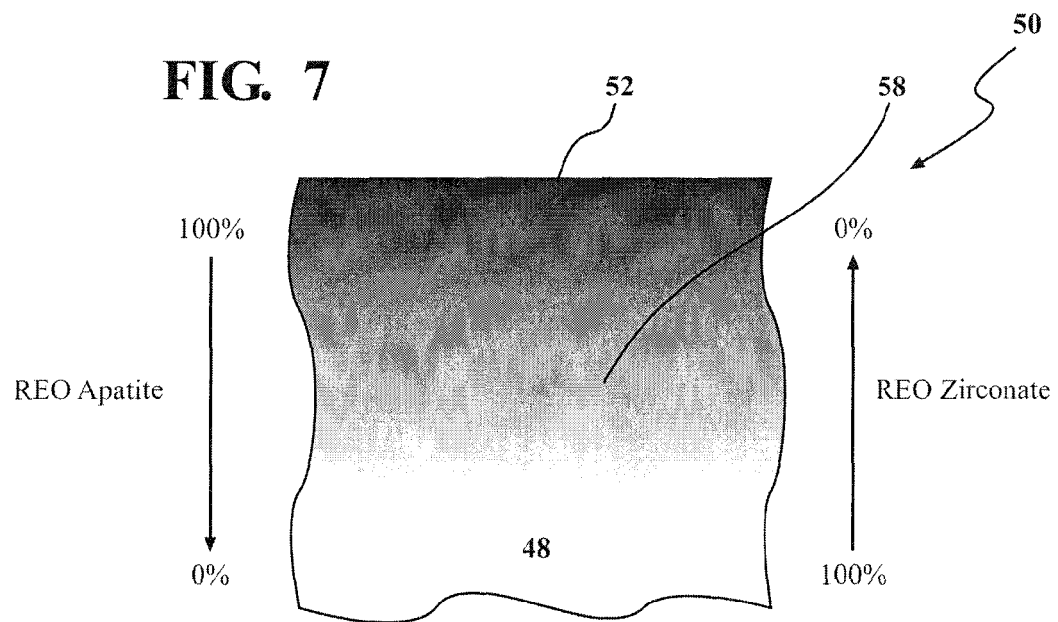
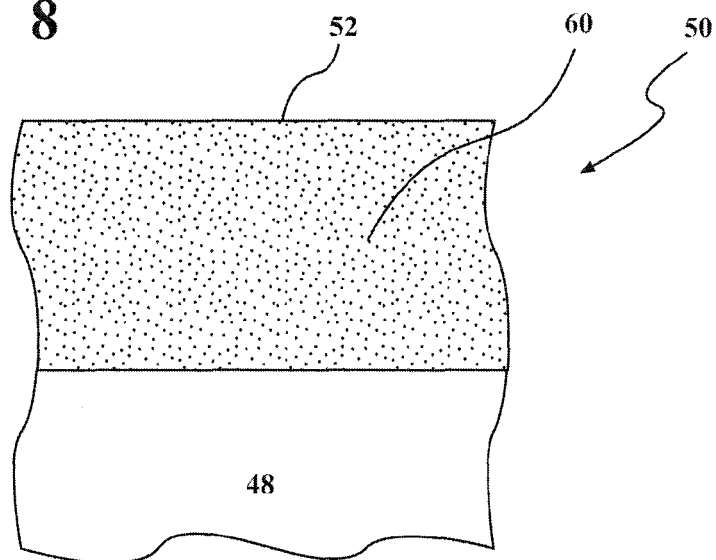
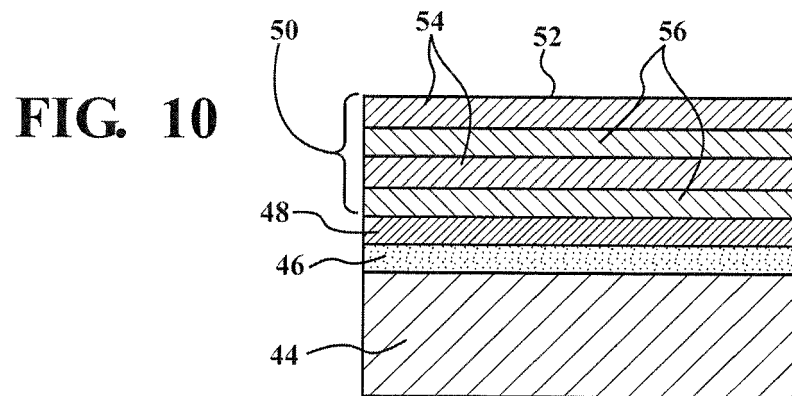
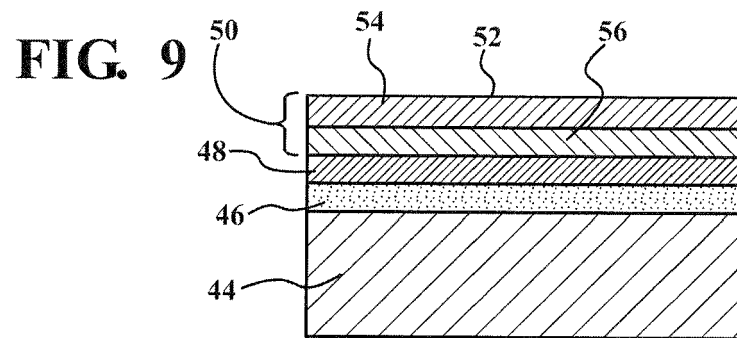


FIG. 8







EUROPEAN SEARCH REPORT

 Application Number
 EP 15 16 8227

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DOCUMENTS CONSIDERED TO BE RELEVANT			
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			C23C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 17 September 2015	Examiner Brisson, Olivier
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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 EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 16 8227

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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