(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 404 127 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
21.11.2018 Bulletin 2018/47

(21) Application number: **18171307.4**

(22) Date of filing: **08.05.2018**

(51) Int Cl.:
C23C 24/04 *(2006.01)* ***C23C 28/00*** *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **08.05.2017 US 201715589553**

(71) Applicant: **United Technologies Corporation**
Farmington, CT 06032 (US)

(72) Inventors:
- **NARDI, Aaron T.**
  East Granby, CT Connecticut 06026 (US)
- **MARTIN, Thomas J.**
  East Hampton, CT Connecticut 06424 (US)
- **STAROSELSKY, Alexander**
  Avon, CT Connecticut 06001 (US)

(74) Representative: **Dehns**
St. Brides House
10 Salisbury Square
London EC4Y 8JD (GB)

(54) FUNCTIONALLY GRADED ENVIRONMENTAL BARRIER COATING

(57) An environmental barrier coating (10) deposited onto a substrate (12) by cold spraying has a microstructure having a porosity (18, 20) that increases through a thickness dimension extending from the substrate (12) toward an outer layer (10n). A process for forming an environmental barrier coating (10) includes sequentially depositing a plurality of layers (10a-10n) of solid powder onto a substrate (12) by cold spraying and heat treating the plurality of layers (10a-10n).

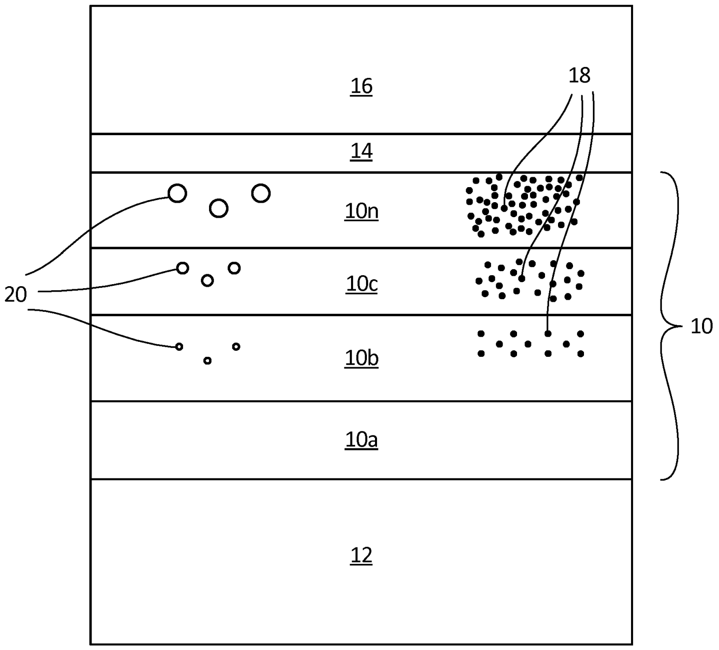

Fig. 1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND

[0001] The present invention relates generally to environmental barrier coatings (EBCs) and more particularly to a process for forming functionally graded EBCs.

[0002] EBCs are used to protect components from environmental attack. EBCs are particularly useful in protecting superalloy components of gas turbine engines exposed to high temperature and corrosive environments. EBCs can consist of intermetallic compounds, such as MCrAlY compounds (where M can be nickel, cobalt, iron, or a mixture thereof). MCrAlY compounds can serve as an aluminum or chromium reservoir to form oxide scales-typically alumina (Al_2O_3) or chromia (Cr_2O_3) at lower temperatures-which act as oxide barriers to protect the metal substrate against oxidation. When placed in an oxygen environment, aluminum and chromium in the EBC diffuses to form oxide scales, collectively referred to as a thermally grown oxide layer (TGO). In the absence of the EBC, oxides would be formed with aluminum or chromium in the substrate, causing degradation of the component over time. In addition to protecting the substrate against oxidation, interdiffusion between the EBC and substrate can improve adherence of the EBC to the substrate.

[0003] In some environments, a thermal barrier coating (TBC) ceramic topcoat can be deposited on top of the EBC to provide thermal insulation for the metal substrate. TBC ceramic topcoats typically consist of yttria, zirconia, gadolinium, and other elements (e.g., yttria-stabilized zirconia (YSZ)), which have a high melting temperature and low thermal conductivity. In TBC systems, the EBC serves as a bond coat, providing the interface between the TBC ceramic topcoat and the metal substrate. Generally, the EBC will share elements with the ceramic topcoat and the metal substrate (e.g., aluminum and yttrium) to form a high strength bond at each interface. While the TBC is resistant to oxidation and corrosion, The TBC allows diffusion of oxygen; therefore, when placed in an oxygen environment, oxygen freely diffuses through the TBC to the EBC where it combines with available aluminum or chromium to form oxides, which develop into the TGO between the EBC and TBC layers.

[0004] During operation, high temperatures and stress can degrade the coating materials, leading to cracking, delamination, and spallation usually at the TBC, EBC, and metal substrate interfaces. A primary contributor to coating degradation is a mismatch of thermal expansion coefficients of the TBC, TGO, EBC, and metal substrate. As the materials cool down, the metal alloy substrate contracts more than the TGO layer between the EBC and TBC. The TGO layer cannot accommodate resulting shear stresses, which causes the formation and growth of cracks in the TGO and delamination of the TGO from the substrate, which can leave the substrate susceptible to degradation.

SUMMARY

[0005] In one aspect, an environmental barrier coating deposited onto a substrate by cold spraying has a microstructure having a porosity that increases through a thickness dimension extending from the substrate toward an outer layer.

[0006] In another aspect, an environmental barrier coating can be formed from a cold spray deposition of elemental metal powders and ceramic powders and diffusion heat treatment of the deposited powders to produce a composite material including an alloy with interspersed ceramic material.

[0007] A process for forming an environmental barrier coating includes sequentially depositing a plurality of layers of solid powder onto a substrate by cold spraying and heat treating the plurality of layers. At least two of the layers have different powder constituents. The cold spraying includes directing the solid powders toward the substrate at a velocity sufficient to cause the solid particles to plastically deform and adhere to the substrate or previously deposited layer.

[0008] The present summary is provided only by way of example, and not limitation. Other aspects of the present disclosure will be appreciated in view of the entirety of the present disclosure, including the entire text, claims and accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

FIG. 1 is a schematic view of a functionally-graded EBC.

FIG. 2 is a flow chart of a process for producing the functionally-graded EBC of FIG. 1.

[0010] While the above-identified figures set forth embodiments of the present invention, other embodiments are also contemplated, as noted in the discussion. In all cases, this disclosure presents the invention by way of representation and not limitation. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the invention. The figures may not be drawn to scale, and applications and embodiments of the present invention may include features, steps and/or components not specifically shown in the drawings.

DETAILED DESCRIPTION

[0011] The present invention combines cold spray material deposition with heat treatment to produce a functionally graded EBC. In one embodiment, the EBC can be functionally graded to increase resistance to erosion and provide thermal protection. In another embodiment, the EBC can be functionally graded to increase strength with a reduction of thermal strain misfit between the substrate and TBC. The EBC can have a graded elastic modulus through a thickness, which can reduce a thermal expansion mismatch between the TBC, EBC, and the substrate. Additionally, a controlled distribution of components of the EBC can reduce thermal cyclic stresses during operation, provide additional structural reinforcement, improve EBC adherence to the substrate, arrest crack propagation, and ultimately enhance the EBC's durability under thermal and structural load cycling.

[0012] Cold spraying, also known as "cold gas dynamic spraying," has been used to form bond coats or EBCs on substrates. Unlike conventional thermal spray processes, cold spraying avoids exposing the substrate to high temperatures. In the cold spray process, solid state powder particles are accelerated toward a substrate at a velocity sufficient to cause the particles to plastically deform upon impact and cold weld or bond to the substrate or a previously deposited layer of powder particles. The particles are not metallurgically transformed in the cold spray process. Conventional cold sprayed EBCs, particularly those designed to serve as bond coats for TBCs, are formed from pre-alloyed powders, such as MCrAlY compounds. Any functional grading is accomplished by varying the chemical composition of the alloyed particles during deposition. No heat treatment is provided. In contrast, the present invention uses the cold spray process to deposit precursor elemental powders, alone or in combination with pre-alloyed powders or powders of other morphologies, which can form a functionally graded EBC upon subsequent diffusion heat treatment. The combination of cold spray and diffusion heat treatment can be used to narrowly control both chemical composition and porosity through a thickness of the EBC to reduce thermal expansion mismatch, improve bond strength, and enhance overall durability and function of the EBC.

[0013] FIGS. 1 and 2 illustrate an EBC of the present invention and a process for forming the EBC. FIG. 1 shows a schematic illustration of EBC 10, having multiple functionally graded layers 10a-10n, substrate 12, TGO 14, and TBC 16. EBC can provide the interface between substrate 12 and TBC 16. In other embodiments, EBC 10 can be applied to substrate 12 without the addition of TBC 16.

[0014] Substrate 12 can be a prefabricated component, including but not limited to components intended to operate within high temperature, thermally cycling, and oxidizing environments. Examples of substrate 12 include a turbine airfoil, combustor liner, and blade outer air seal in a gas turbine engine. Substrate 12 can be made of a superalloy material, including but not limited to a nickel superalloy. In some embodiments, substrate 12 can be a single-crystal nickel-aluminum superalloy formed by investment casting, directional solidification, equiax direct build, forging, additive manufacturing, or other processes known in the art. It will be understood by one of ordinary skill in the art that EBC 10 and the process of forming EBC 10 disclosed in the present invention can be used for a variety of material substrates and applications. While the present disclosure is directed to an example of the production of an ECB for use on a component within a hot section of a gas turbine engine, the disclosed ECB and process of formation can be adapted for use on a variety of components and within a variety of environments.

[0015] EBC 10 can be formed from the cold spray deposition of multiple layers 10a-10n of solid powder particles, generally including but not limited to metals, intermetallics, or alloys. For thermal protection applications, EBC 10 can generally consist of an intermetallic compound, such as an MCrAlY (where M is nickel, cobalt, iron, or mixtures thereof) or platinum aluminide. Although the number of layers 10a-10n and thickness (extending from substrate 12 to TBC 16 in FIG. 1) of EBC 10 can be varied, functionally graded EBC 10 can generally include three to five layers 10a-10n, forming a coating having a thickness between 75 μm and 200 μm with each layer 10a-10n having a thickness of approximately 25 μm. EBC 10 can be functionally graded by modifying the cold spray process and feedstock material layer-by-layer. In embodiments requiring narrow functional grading, EBC 10 can have more than five layers 10a-10n and, in some cases, can have more than 20 layers 10a-10n. It will be understood by one of ordinary skill in the art that the thickness of each layer 10a-10n and number of layers 10a-10n can be changed by modifying spray parameters and material feedstock (e.g., nozzle traverse speed, powder feed rate, powder size, etc.).

[0016] Functional grading can be accomplished by selecting precursor powders for each layer 10a-10n to provide a gradual transition in the microstructure between each layer 10a-10n and between substrate 12 and optional TBC 16 following subsequent diffusion heat treatment. Precursor powders can vary widely in chemical composition, morphology, and particle size, with a typical size ranging from 5 μm to 70 μm. Precursor powders can be pre-mixed at engineered compositions and delivered to the spray gun from a single storage container (e.g., hopper) or can be individually fed as homogeneous compositions or elemental powders from separate storage containers. Powders can be simultaneously fed to the spray gun from multiple storage containers at the same or differing powder feed rate, as set to optimize mixing, or can be fed from multiple storage containers on an alternating basis (e.g., alternating with each layer 10a-10n). The precursor powders can be delivered through a powder feeder to the cold spray gun where the powder converges with a compressed gas stream, is accelerated, and is delivered to substrate 14 or a previously deposited layer 10a-10n.

[0017] By finely selecting and controlling the deposition of precursor powders layer-by-layer, graduated mixing regions can be developed between and within each layer 10a-10n of EBC 10 to optimize functional gradation of EBC 10 through the thickness of EBC 10 extending from substrate 12 to optional TBC 16 upon diffusion heat treatment. In this manner, the microstructure and chemical composition of each layer 10a-10n can be finely controlled. For instance, a porosity (illustrated by reference numbers 18 (varying in pore quantity) and 20 (varying in pore size) in FIG. 1) can be tailored to provide a graded elastic modulus and thermal expansion coefficient through the thickness of EBC 10 thereby reducing the thermal strains between the substrate 12, EBC 10, and TBC 16; while a varying content of oxide-forming elements (e.g., aluminum) can be tailored to control TGO growth.

[0018] Areas of highest stress are generally located at the interface between EBC 10 and TBC 16, as the thermal expansion coefficient of EBC 10 can be typically be two times greater than the thermal expansion coefficient of TBC 16. The thermal expansion coefficient and elastic modulus of EBC 10, and particularly outermost layer 10n, can be reduced to more closely match that of TBC 16. A reduction in the elastic modulus can generally be achieved by increasing the porosity of the layer 10a-10n. The porosity can be created and tailored, with regard to both volume and pore size, through the thickness of EBC 10 (layers 10a-10n) by controlling the proportion of pre-alloyed versus elemental powder deposited and/or by controlling the powder morphology.

[0019] During heat treatment, a diffusing species can cause the formation of pores in the microstructure. For example, aluminum, which has a relatively low melting point, can diffuse at lower temperatures than some other metals. When combined with nickel in a controlled thermal process, aluminum will diffuse into the nickel leaving a pore where the aluminum was. The size and location of the primary diffusing species, as well as diffusion time, are critical to the formation and extent of the porosity. Porosity can be increased in each layer 10a-10n by increasing the amount of elemental aluminum or other diffusing species deposited. As shown in FIG. 1, porosity can increase through the thickness of EBC 10, extending from substrate 12 to TBC 16. In some embodiments, innermost layer 10a can have essentially no porosity or a porosity of less than two percent, which is consistent with the porosity of substrate 12, while outermost later 10n can have a porosity greater than 10 percent and, in some embodiments, between 20 and 50 percent nearest TBC 16 and thereby reduce the strain caused by thermal coefficient mismatch between EBC 10 and TBC 16.

[0020] The size and shape of the pores can also be tailored by controlling the size and shape of the diffusing species, which can be accomplished through the selection of powder morphology, powder constituents, and spray parameters. For example, a layer 10a-10n formed by the deposition of a blend of pre-alloyed NiCrAlY powders and elemental aluminum can result in the formation of thin pores following diffusion heat treatment. In this case, the thin pores are caused by the flattening of the elemental aluminum during deposition. Because the particle velocity required to deposit pre-alloyed NiCrAlY powder onto substrate 12 is greater than the velocity required to deposit elemental aluminum, the increased particle velocity causes the aluminum to flatten upon impact. During heat treatment, the elemental aluminum diffuses leaving behind a flattened pore in the shape of the originally deposited elemental aluminum powder. In contrast, a layer 10a-10n formed by the deposition of nickel clad aluminum powders can result in the formation of spherical or semi-spherical pores, resultant of reduced particle deformation. The nickel clad aluminum particles can require a particle velocity similar to that of NiCrAlY particles for deposition, however, the elemental aluminum can largely be protected from deformation by the outer nickel layer upon impact. During a controlled heat treatment, the aluminum can diffuse into the nickel leaving behind a hollow nickel aluminum structure, which can have an inner pore shape and size approximately equal to that of the aluminum in the precursor powder. As a whole, the plurality of nickel clad aluminum powders can form a closed cell foam structure upon diffusion heat treatment. The size of the pores obtained with clad composite, such as nickel clad aluminum, can be significantly larger than those obtained with blended powders that include elemental aluminum.

[0021] The aluminum in typical nickel clad aluminum powders has a minimum diameter of around 30 μm as compared to 1-2 μm for elemental aluminum powders. As shown in FIG. 1, the size of the pores can be tailored to increase in outermost layer 10n. In some embodiments, an increase in pore size at outmost layer 10n can increase surface roughness and improve bonding between EBC 10 and TBC 16. It will be understood by one of ordinary skill in the art that the blended powders can include a variety of alloys and elemental powders not limited to NiCrAlY and elemental aluminum. Similarly, it will be understood that clad composites are not limited to nickel clad aluminum, although the benefits of elemental aluminum in a functionally graded bond coat-as a diffusing species and an oxide-forming element-will be recognized.

[0022] Given the teachings provided herein, it will be understood by one of ordinary skill in the art to vary chemical composition, morphology, and size of precursor powder particles to achieve a microstructure of optimally graded porosity through the thickness of EBC 10. In addition to the blended powders and clad composites discussed above, granulated composite, spray dried composite, and mechanically alloyed powders can produce unique microstructures and can be used to finely control the porosity of EBC layers 10a-10n. While FIG. 1 illustrates increasing porosity through layers 10a-10n by both increasing a quantity of similarly sized pores 18 (illustrated by reference number 18) and increasing a size of pores (illustrated by reference number 20), it will be understood that either or both increased quantity and size can be suitable for producing a graded elastic modulus through the thickness of EBC 10 for reducing thermal expansion mismatch.

[0023] The chemical composition of EBC 10 can also be varied to control TGO formation and growth and to enhance EBC 10 strength. For example, the content of oxide-forming elements, such as aluminum, can be increased by weight percent in outermost layer 10n to provide a reservoir of aluminum available for TGO growth. Aluminum content can also be decreased in innermost layer 10a and other layers near substrate 12 to minimize inward diffusion of aluminum, which can damage substrate 12. In general, aluminum content in innermost layer 10a can approximately match an aluminum content in substrate 12 to limit aluminum diffusion in either direction between substrate 12 and EBC 10.

[0024] In other embodiments, EBC 10, particularly when used in the absence of TBC 16, can be functionally graded to increase resistance to erosion due to particle impact and to provide thermal protection. The cold spray plus diffusion heat treatment process can be used to optimize the chemical composition and functionality of EBC 10 to produce an EBC 10 capable of providing thermal protection to substrate 12 without a TBC 16 topcoat. For example, the cold spray deposition of elemental particles and metal clad ceramics can provide for tailored alloy formation and optimized interspersion of ceramic material upon diffusion heat treatment.

[0025] It will be understood by one of ordinary skill in the art that the microstructure and chemical composition of EBC 10 can be finely adapted to accommodate the needs of varying applications and that it is the combination of finely controlled particle deposition and diffusion through heat treatment that can optimize the function of EBC 10. Furthermore, it will be understood that the disclosed process can be extended to other common EBCs, such as yttrium silicate, which includes a reaction silicon barrier and a silicon carbide bond coat.

[0026] In some embodiments, particularly those designed for high temperature environments, TBC 16 can be applied over EBC 10. TBC 16 can be a ceramic topcoat, such as YSZ or similar high temperature ceramic capable of providing thermal or environmental barrier protection. Suitable ceramics can include but are not limited to zirconia, alumina, gadolinium zirconia, silica, titania, yttria, boron nitride, carbon nitride, silicon nitride, silicon carbide, tantalum carbide, and tungsten carbide. TBC 16 can be deposited on EBC 10 using deposition processes known in the art, including but not limited to, thermal spray, chemical vapor deposition (CVD), and physical vapor deposition (PVD). Examples of thermal spray deposition include air plasma spray (APS), suspension plasma spray (SPS), solution precursor plasma spray (SPPS), low pressure plasma spray (LPPS), and high velocity oxygen fuel (HVOF). Examples of PVD include cathodic arc (Arc-PVD) and electron beam physical vapor deposition (EB-PVD). TBC 16 can typically have a thickness ranging from 100 μm - 400 μm, but can be varied outside of this range depending on the application. Depending on the deposition process, TBC 16 can have a variety of defining microstructures, including but not limited to elongated columnar grains (consistent with EB-PVD), columnar structures formed by preferential deposition (consistent with SPS, SPPS), lamellar structures (consistent with APS), and dense vertical cracked structures with columnar or equiaxed grains consistent with APS, SPS, SPPS). It will be understood by one of ordinary skill in the art to tailor EBC 10 in accordance with the microstructure of or deposition method used to form TBC 16 to optimize bond strength or other interfacial properties.

[0027] FIG. 2 illustrates the process for forming EBC 10, which includes cold spray deposition (step 28) followed by a controlled diffusion heat treatment process (step 30). The cold spray deposition process includes selecting a precursor powder composition for each ECB layer 10a-10n (step 32) and depositing each EBC layer 10a-10n (step 34) in a layer-by-layer fashion using a cold spray technique as known in the art. The steps of powder selection (step 32) and deposition (step 34) can repeat until all ECB layers 10a-10n have been deposited. As previously discussed, precursor powders can be premixed in a single hopper or can be fed from multiple hoppers with a controlled feed rate and mixed in the gas stream. The powder particles can be accelerated to supersonic speeds by compressed gas, such as helium, nitrogen, other inert gases, or combinations thereof. Conventional cold sprayed MCrAlY coatings generally require helium to accelerate the particles to a velocity sufficient for deposition. Nitrogen gas can be more cost effective, but is generally not capable of producing the requisite particle velocity for alloyed particles having high hardness. Nitrogen can be suited for the cold spray deposition of softer elemental powders and can be utilized for various embodiments of the present invention. EBCs 10 produced from the blending of elemental powders or other soft particles can, therefore, reduce processing costs over conventional MCrAlY cold sprayed EBCs.

[0028] Following deposition of outermost EBC layer 10n, EBC 10 is exposed to the controlled diffusion heat treatment process (step 30). Controlled heat treatment causes interdiffusion of elements in EBC layers 10a-10n and diffusion of elements of EBC 10 with elements of substrate 12. The interdiffusion of elements within EBC layers 10a-10n can create the graded porosity through the thickness of EBC 10. The diffusion of elements in EBC 10 with elements of substrate 12 can create a diffusion bond joint, which can enhance the bond between EBC 10 and substrate 12. Heat treatment can be carried out using conventional heat treatment systems known in the art (e.g., high vacuum furnace or argon atmosphere furnace), in which the component including EBC 10 is heated.

[0029] In some embodiments, the heat treatment process (step 30) can be divided into multiple steps of applying heat to EBC 10 (step 38) and holding EBC 10 at a preselected temperature (step 40) to control diffusion and porosity formation. The steps of applying heat and holding at temperature can be repeated until a maximum holding temperature reaches (or exceeds) a minimum diffusion bonding temperature of the innermost EBC layer 10a. (e.g., approximately 1200 °C for a layer 10a formed from a NiCrAlY alloy), while remaining below a melting point of the EBC layer 10a-10n having the lowest melting point after chemistry homogenization to prevent incipient melting. The lowest melting point can be determined by depositing each layer 10a-10n on a separate coupon, heat treating to form an alloy of the deposited powders, and analyzing each EBC layer 10a-10n using methods known in the art (e.g., differential scanning calorimetry) to determine the melting points.

[0030] It will be understood by one of ordinary skill in the art that the diffusion heat treatment process can be tailored based on the chemical constituents of EBC 10 and may require a slow increase in temperature to limit exothermic reactions between particular constituents (e.g., aluminum and nickel). Hold times and temperatures and ramp-up rates can vary depending on the chemical composition. Modeling or experimentation can be used to optimize the diffusion heat treatment process. In order to reduce the processing time, modeling or experimentation can be used to determine the temperature at which an exothermic reaction is observed, which indicates that diffusion is occurring too rapidly and can result in an unstable accelerated process. A hold temperature can generally be set 50-100 °C below the temperature at which an exothermic reaction will occur to allow optimal diffusion. After this point, it may be possible to heat to the final temperature. Other materials may require multiple hold times. In one nonlimiting example of experimental optimization, EBC 10 (including substrate 12) was heated to 400 °C at a rate of 2 °C per minute and then held at 400 °C for two hours. Thereafter, the temperature was increased at a rate of 2 °C per minute and at held for period for two hours at 450 °C, 500 °C, 550 °C, 600 °C, 800 °C, and 1000 °C before being heated to a final temperature of 1200 °C. Methods known in the art, including differential scanning calorimetry or thermogravimetric analysis, can be used to monitor exothermic processes.

[0031] In some embodiments, TBC 16 topcoat can be deposited on EBC 10 following heat treatment (step 44). As previously discussed, the TBC 16 can be deposited using any material deposition process known in the art, including but not limited to, thermal spray, CVD, and PVD methods. It will be understood by one of ordinary skill in the art to tailor EBC 10 in accordance with the microstructure of or deposition method used to form TBC 16 to optimize bond strength or other interfacial properties. In some embodiments, a surface of EBC 10 can be prepared for TBC 16 deposition. Surface preparation methods can include but are not limited to peening and grit blasting to provide a surface roughness optimized for deposition of TBC 16.

[0032] The combination of cold spray material deposition with diffusion heat treatment can be used to produce a functionally graded EBC having increased strength and resistance to erosion, thermal protection, and a reduction of thermal strain misfit between the substrate and a TBC topcoat. The EBC can have a graded elastic modulus through a thickness, which can reduce a thermal expansion mismatch between the TBC, EBC, and the substrate. Additionally, a controlled distribution of components of the EBC can reduce thermal cyclic stresses during operation, provide additional structural reinforcement, improve EBC adherence to the substrate, arrest crack propagation, and ultimately enhance the EBC's durability under thermal and structural load cycling.

Discussion of Possible Embodiments

[0033] The following are non-exclusive descriptions of possible embodiments of the present invention.

[0034] An environmental barrier coating deposited onto a substrate by cold spraying has a microstructure having a porosity that increases through a thickness dimension extending from the substrate toward an outer layer.

[0035] The environmental barrier coating of the preceding paragraph can optionally include, additionally and/or alternatively, any one or more of the following features, configurations and/or additional components:

A further embodiment of the foregoing environmental barrier coating can further include a chemical composition having a content of an oxide-forming element increasing in weight percent toward the outer layer.

[0036] A further embodiment of any of the foregoing environmental barrier coatings, wherein the microstructure can be formed from a powder with morphology selected from the group consisting of clad composite, granulated composite, spray dried composite, blended, and mechanically alloyed particles.

[0037] A further embodiment of any of the foregoing environmental barrier, wherein the microstructure can be formed from elemental metal powders.

[0038] A further embodiment of any of the foregoing environmental barrier coatings, wherein the porosity of the microstructure is formed upon post-deposition diffusion heat treatment of the powders.

[0039] A further embodiment of any of the foregoing environmental barrier coatings, wherein the microstructure can include hollow nickel aluminum structures.

[0040] A further embodiment of any of the foregoing environmental barrier coatings, wherein the porosity of the microstructure in the outer layer can be equal to or greater than 10 percent.

[0041] A further embodiment of any of the foregoing environmental barrier coatings, wherein the porosity of the microstructure at an inner layer adjacent the substrate can be equal to or less than two percent.

[0042] A further embodiment of any of the foregoing environmental barrier coatings, wherein an elastic modulus of the coating can successively increase layer-by-layer from the substrate to the outer layer.

[0043] An environmental barrier coating is formed from a cold spray deposition of elemental metal powders and ceramic powders and diffusion heat treatment of the deposited powders to produce a composite material including an alloy with interspersed ceramic material.

[0044] The environmental barrier coating of the preceding paragraph can optionally include, additionally and/or alternatively, any one or more of the following features, configurations and/or additional components:

A further embodiment of the foregoing environmental barrier coating, wherein the environmental barrier coating can be formed by cold-spraying metal clad ceramic powders.

[0045] Also provided is a component, such as a component for use in a high temperature, thermally cycling and/or oxidizing environment, comprising a substrate coated with an environmental barrier coating as described in any of the above, or as claimed.

[0046] A process for forming an environmental barrier coating includes the steps of sequentially depositing a plurality of layers of solid powder onto a substrate by cold spraying and heat treating the plurality of layers. At least two of the layers comprise different powder constituents. The cold spraying comprises directing the solid powders toward the substrate at a velocity sufficient to cause the solid particles to plastically deform and adhere to the substrate or previously deposited layer.

[0047] The process of the preceding paragraph can optionally include, additionally and/or alternatively, any one or more of the following features, configurations, components, and/or additional steps:

A further embodiment of the foregoing process, wherein sequentially depositing the plurality of layers can include cold-spraying powders selected from the group consisting of elemental powders, fully alloyed powders, blended powders, clad composite powders, granulated composite powders, spray dried powders, and mechanical alloyed powders.

[0048] A further embodiment of any of the foregoing processes, wherein sequentially depositing the plurality of layers can further include successively increasing an amount of an oxide-forming element in the plurality of layers.

[0049] A further embodiment of any of the foregoing processes can further include cold-spraying powders selected from the group consisting of elemental aluminum and nickel clad aluminum.

[0050] A further embodiment of any of the foregoing processes can further include cold-spraying metal clad ceramic powders.

[0051] A further embodiment of any of the foregoing processes, wherein the solid powders can be accelerated in a nitrogen working gas.

[0052] A further embodiment of any of the foregoing processes, wherein heat treating the plurality of layers can include increasing a furnace temperature at a substantially constant rate and holding the temperature constant for a predetermined period of time. The furnace temperature and holding temperature can be determined based on a melting point of each alloyed or elemental constituent within the powder. The maximum hold temperature can be approximately equal to or greater than the minimum diffusion bonding temperature of a coating layer nearest the substrate and can be below a melting point of a coating layer having the lowest melting point after chemistry homogenization.

[0053] A further embodiment of any of the foregoing processes, wherein heat treating can further include forming a microstructure having a porosity that increases through a thickness dimension of the environmental barrier coating extending from the substrate to an outer layer of the coating.

[0054] A further embodiment of any of the foregoing processes, wherein the porosity can successively increase through each of the plurality of layers.

[0055] A further embodiment of any of the foregoing processes, wherein heat treating can further include forming pores in the outer layer of the coating having a larger diameter than pores formed in inner layers of the coating.

[0056] A further embodiment of any of the foregoing processes can further include depositing a ceramic layer on the outer layer of the coating following heat treatment.

[0057] A further embodiment of any of the foregoing processes, wherein heat treating can further include diffusion bonding the coating to the substrate.

Summation

[0058] Any relative terms or terms of degree used herein, such as "substantially", "essentially", "generally", "approximately" and the like, should be interpreted in accordance with and subject to any applicable definitions or limits expressly stated herein. In all instances, any relative terms or terms of degree used herein should be interpreted to broadly encompass any relevant disclosed embodiments as well as such ranges or variations as would be understood by a person of ordinary skill in the art in view of the entirety of the present disclosure, such as to encompass ordinary manufacturing tolerance variations, incidental alignment variations, transient alignment or shape variations induced by thermal, rotational or vibrational operational conditions, and the like. Moreover, any relative terms or terms of degree used herein should be interpreted to encompass a range that expressly includes the designated quality, characteristic, parameter or value, without variation, as if no qualifying relative term or term of degree were utilized in the given disclosure or recitation.

[0059] While the invention has been described with reference to an exemplary embodiment(s), it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment(s) disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.

Claims

1. An environmental barrier coating (10) deposited onto a substrate (12) by cold spraying, the environmental barrier coating (10) comprising a microstructure having a porosity (18, 20) that increases through a thickness dimension extending from the substrate (12) toward an outer layer (10n).

2. The environmental barrier coating (10) of claim 1, wherein the environmental barrier coating (10) comprises a chemical composition comprising an oxide-forming element increasing in weight percent toward the outer layer (10n).

3. The environmental barrier coating (10) of claim 1 or 2, wherein the microstructure is formed from:

   a powder with morphology selected from the group consisting of clad composite, granulated composite, spray dried composite, blended, and mechanically alloyed particles; or
   elemental metal powders.

4. The environmental barrier coating (10) of claim 1, 2 or 3, wherein the microstructure comprises hollow nickel aluminum structures.

5. The environmental barrier coating (10) of any preceding claim, wherein the porosity (18, 20) of the microstructure in the outer layer (10n) is equal to or greater than 10 percent.

6. The environmental barrier coating (10) of any preceding claim, wherein the porosity (18, 20) of the microstructure at an inner layer (10a) adjacent the substrate (12) is equal to or less than two percent.

7. The environmental barrier coating (10) of any preceding claim, wherein an elastic modulus of the coating successively increases layer-by-layer from the substrate (12) to the outer layer (10n).

8. A process for forming an environmental barrier coating (10) comprising the steps of:

   sequentially depositing a plurality of layers (10a-10n) of solid powder onto a substrate (12) by cold spraying, wherein at least two of the layers (10a-10n) comprise different powder constituents; and
   heat treating the plurality of layers (10a-10n), wherein cold spraying comprises directing the solid powders toward the substrate (12) at a velocity sufficient to cause the solid powders to plastically deform and adhere to the substrate (12) or previously deposited layer (10a-10n).

9. The process of claim 8, wherein the solid powders are selected from the group comprising elemental powders, fully alloyed powders, blended powders, clad composite powders, granulated composite powders, spray dried powders, mechanical alloyed powders, and combinations thereof.

10. The process of claim 8 or 9, wherein sequentially depositing the plurality of layers (10a-10n) further comprises successively increasing an amount of an oxide-forming element in the plurality of layers (10a-10n).

11. The process of claim 8, 9 or 10, wherein the solid powders comprise powders selected from the group consisting of elemental aluminum and nickel clad aluminum.

12. The process of claim 8, 9 or 10, wherein the solid powders comprise metal clad ceramic powders.

13. The process of any preceding claim, wherein heat treating the plurality of layers (10a-10n) comprises:

    increasing a furnace temperature at a substantially constant rate; and
    holding the temperature constant for a predetermined period of time, wherein each of the furnace temperature and holding temperature is determined based on a melting point of each alloyed or elemental constituent within the powder, and the maximum hold temperature is equal to or greater than the minimum diffusion bonding temperature of a coating layer (10a) nearest the substrate (12) and is below a melting point of a coating layer (10a-10n) having the lowest melting point layer chemistry homogenization.

14. The process of any preceding claim, wherein heat treating further comprises forming pores (20) in the outer layer (10a) of the coating (10) having a larger diameter than pores (20) formed in inner layers (10a, 10b, 10c) of the coating (10).

15. The process of any preceding claim, wherein heat treating further comprises forming a microstructure having a porosity (18, 20) that increases through a thickness dimension of the environmental barrier coating (10) extending from the substrate (12) to an outer layer (12) of the coating (10).

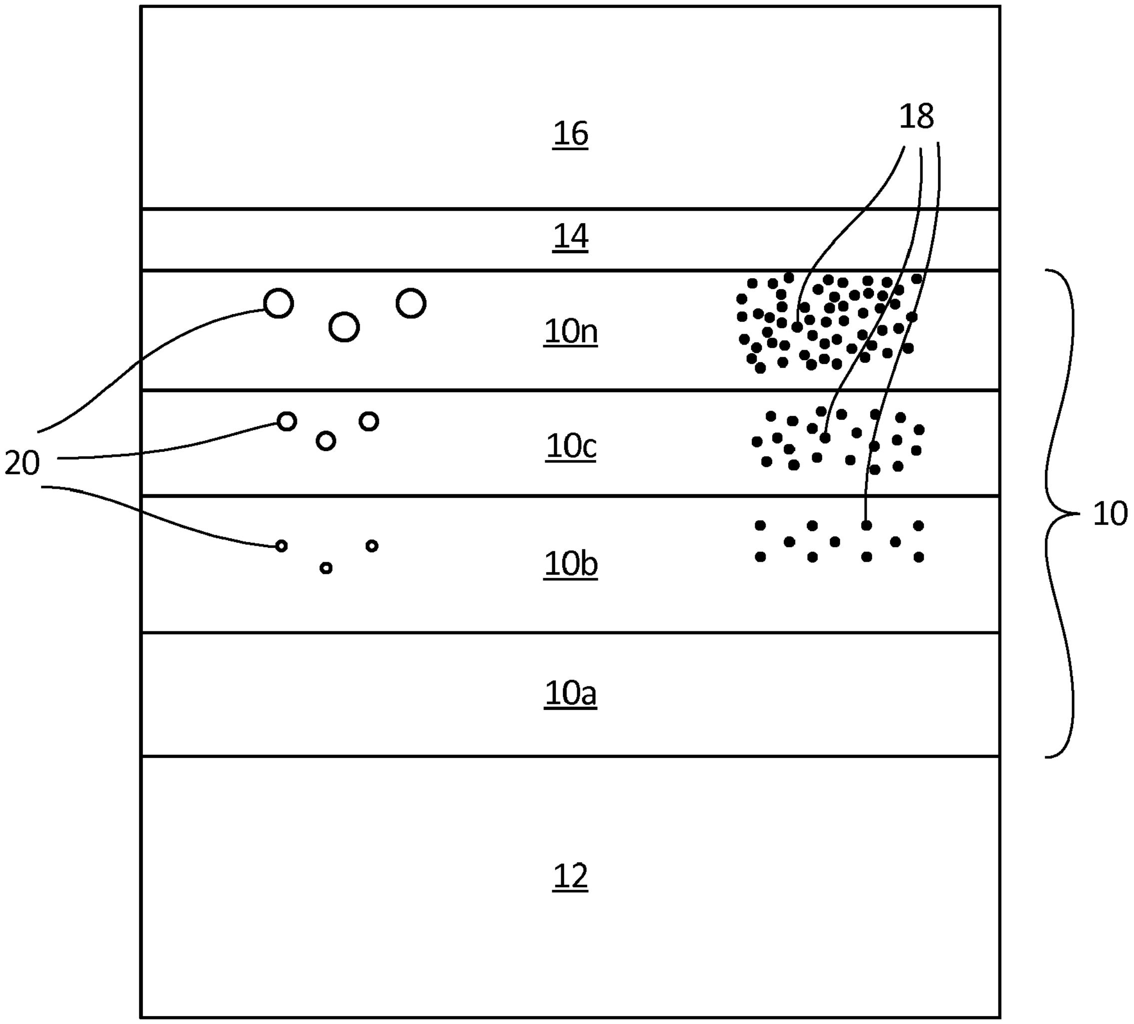

Fig. 1

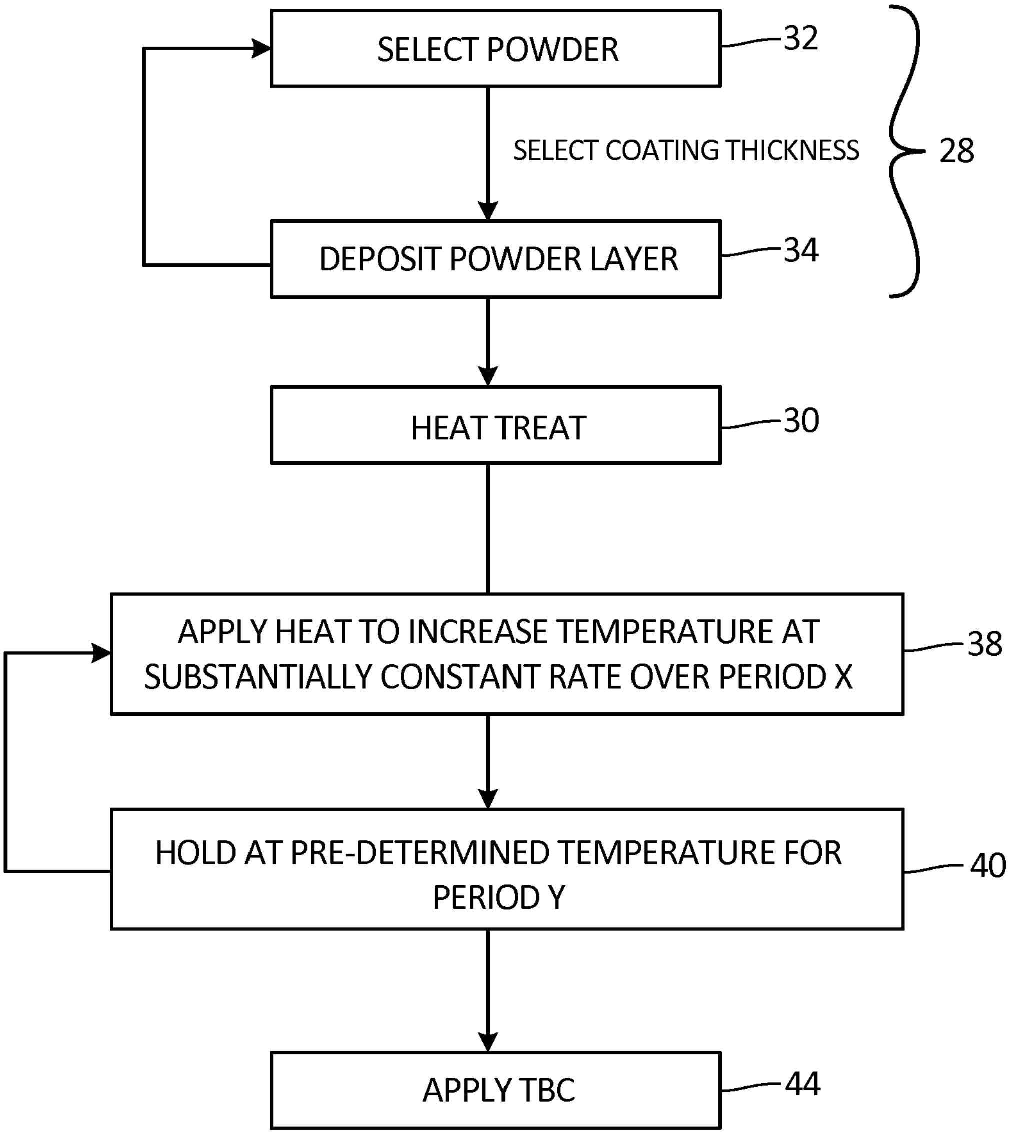
SELECT POWDER
32
SELECT COATING THICKNESS
28
DEPOSIT POWDER LAYER
34
HEAT TREAT
30
APPLY HEAT TO INCREASE TEMPERATURE AT SUBSTANTIALLY CONSTANT RATE OVER PERIOD X
38
HOLD AT PRE-DETERMINED TEMPERATURE FOR PERIOD Y
40
APPLY TBC
44

Fig. 2

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 17 1307

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 2 617 869 A2 (GEN ELECTRIC [US]) 24 July 2013 (2013-07-24) * paragraphs [0027] - [0031]; claims * -----	1-3, 8-12,14, 15	INV. C23C24/04 C23C28/00
X	US 2007/098912 A1 (RAYBOULD DEREK [US] ET AL) 3 May 2007 (2007-05-03) * paragraphs [0014] - [0026]; claims * -----	8,9,13	
X	EP 1 382 707 A1 (SIEMENS AG [DE]) 21 January 2004 (2004-01-21) * paragraphs [0012] - [0020]; claims * -----	1-3,5-15	
A	EP 2 072 634 A2 (UNITED TECHNOLOGIES CORP [US]) 24 June 2009 (2009-06-24) * claims * -----	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C23C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	21 September 2018	Mauger, Jeremy

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

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

EP 18 17 1307

21-09-2018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2617869 A2	24-07-2013	EP 2617869 A2	24-07-2013
		JP 2013146728 A	01-08-2013
		RU 2013102141 A	27-07-2014
		US 2013186304 A1	25-07-2013
US 2007098912 A1	03-05-2007	NONE	
EP 1382707 A1	21-01-2004	EP 1382707 A1	21-01-2004
		WO 2004007787 A1	22-01-2004
EP 2072634 A2	24-06-2009	EP 2072634 A2	24-06-2009
		SG 153768 A1	29-07-2009
		US 2011305892 A1	15-12-2011
		US 2012196151 A1	02-08-2012