ARTICLES FOR HIGH TEMPERATURE SERVICE

Articles having coatings that are resistant to high temperature degradation are described, along with methods for making such articles. The article (100) comprises a coating (110) disposed on a substrate (120). The coating (110) comprises a plurality of elongated surface-connected voids (130). The article (100) further includes a protective agent (150) disposed within at least some of the voids (130) of the coating (110); the protective agent (150) comprises a substance capable of chemically reacting with liquid nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS. This solid crystalline product has a melting temperature greater than about 1200 degrees Celsius. The method generally includes disposing the protective agent (150) noted above within the surface connected voids (130) of the coating (110) at an effective concentration to substantially prevent incursion of CMAS materials into the voids (130) in which the protective agent (150) is disposed.
BACKGROUND

[0001] This disclosure generally relates to articles employing thermally protective coatings. More particularly, this disclosure relates to articles employing coatings that are resistant to degradation due to high-temperature interactions with dust materials.

[0002] Thermal barrier coatings are typically used in articles that operate at or are exposed to high temperatures. Aviation turbines and land-based turbines, for example, may include one or more components protected by the thermal barrier coatings. Under normal conditions of operation, coated components may be susceptible to various types of damage, including erosion, oxidation, and attack from environmental contaminants.

[0003] For turbine components, environmental contaminant compositions of particular concern are those containing oxides of calcium, magnesium, aluminum, silicon, and mixtures thereof; dirt, ash, and dust ingested by gas turbine engines, for instance, are often made up of such compounds. These oxides often combine to form contaminant compositions comprising mixed calcium-magnesium-aluminum-silicon-oxide systems (Ca-Mg-Al-Si-O), hereafter referred to as "CMAS." At the high turbine operating temperatures, these environmental contaminants can adhere to the hot thermal barrier coating surface, and thus cause damage to the thermal barrier coating. For example, CMAS can form compositions that are liquid or molten at the operating temperatures of the turbines. The molten CMAS composition can dissolve the thermal barrier coating, or can fill its porous structure by infiltrating the pores, channels, cracks, or other cavities in the coating. Upon cooling, the infiltrated CMAS composition solidifies and reduces the coating strain tolerance, thus initiating and propagating cracks that may cause delamination and spalling of the coating material. This may further result in partial or complete loss of the thermal protection provided to the underlying metal substrate of the part or component. Further, spallation of the thermal barrier coating may create hot spots in the metal substrate leading to premature component failure. Premature component failure can lead to unscheduled maintenance as well as parts replacement resulting in reduced performance, and increased operating and servicing costs.

[0004] Thus, there is a need for improved coating systems that provide protection to thermal barrier coatings from the adverse effects of environmental contaminants, when operated at or exposed to high temperatures. In particular, there is a need for improved coating systems, and methods for making such coatings, that provide protection from the adverse effects of deposited CMAS.

BRIEF DESCRIPTION

[0005] Embodiments of the present invention are provided to meet this and other needs. One embodiment is an article that comprises a coating disposed on a substrate. The coating comprises a plurality of elongated surface-connected voids. The article further includes a protective agent disposed within at least some of the voids of the coating; the protective agent comprises a substance capable of chemically reacting with liquid nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS. This solid crystalline product has a melting temperature greater than about 1200 degrees Celsius.

[0006] Another embodiment is a method for making articles such as the article described above. The method generally includes disposing the protective agent noted above within the surface connected voids of the coating at an effective concentration to substantially prevent incursion of CMAS materials into the voids in which the protective agent is disposed. More particularly, the method includes disposing a protective agent within a plurality of elongated surface-connected voids of a coating; wherein the protective agent comprises a substance capable of chemically reacting with nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS, wherein the solid crystalline product has a melting temperature greater than about 1200 degrees Celsius, and wherein the protective agent is present in the coating in an effective concentration to substantially prevent incursion by said nominal CMAS into voids in which the protective agent is disposed.

DRAWINGS

[0007] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawing in which like characters represent like parts, wherein:

Figure 1 is a schematic cross-section illustrating one embodiment of the present invention; and

Figure 2 is a schematic cross-section illustrating another embodiment of the present invention.
Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about", and "substantially" is not to be limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Here and throughout the specification and claims, range limitations may be combined and/or interchanged; such ranges are identified and include all the sub-ranges contained therein unless context or language indicates otherwise.

In the following specification and the claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. As used herein, the term "or" is not meant to be exclusive and refers to at least one of the referenced components being present and includes instances in which a combination of the referenced components may be present, unless the context clearly dictates otherwise.

As used herein, the terms "may" and "may be" indicate a possibility of an occurrence within a set of circumstances; a possession of a specified property, characteristic or function; and/or qualify another verb by expressing one or more of an ability, capability, or possibility associated with the qualified verb. Accordingly, usage of "may" and "may be" indicates that a modified term is apparently appropriate, capable, or suitable for an indicated capacity, function, or usage, while taking into account that in some circumstances, the modified term may sometimes not be appropriate, capable, or suitable.

As used herein, the term "coating" refers to a material disposed on at least a portion of an underlying surface in a continuous or discontinuous manner. Further, the term "coating" does not necessarily mean a uniform thickness of the disposed material, and the disposed material may have a uniform or a variable thickness. The term "coating" may refer to a single layer of the coating material or may refer to a plurality of layers of the coating material. The coating material may be the same or different in the plurality of layers.

Embodiments of the present invention incorporate a coating that includes one or more substances, referred to herein collectively as "protective agents," disposed within spaces in the coating, that is, surface-connected voids such as cracks, pores, voids, and the like, through which molten CMAS typically infiltrate the coating and ultimately degrade it as described previously. A protective agent is designed to be highly reactive to CMAS-type material, such that, at typical temperatures where CMAS is encountered in liquid form, the protective agent rapidly reacts with the CMAS to form a solid reaction product that itself is thermally and chemically stable in the presence of liquid CMAS, forming a solid-phase barrier against further CMAS ingress.

To perform the function described above, a "protective agent" includes a substance that is reactive with CMAS material. More particularly, a substance is considered suitable as a substance for use in the protective agent as described herein if the substance has the characteristic property, that is, the capability, of chemically reacting with a nominal CMAS liquid composition at atmospheric pressure to form a solid, crystalline product that is outside the crystallization field of this nominal CMAS composition. The solid crystalline product has a higher melting temperature than the nominal CMAS composition so that it remains as a solid barrier to liquid infiltration. For the purposes of this description, the term "nominal CMAS" refers to the following composition, with all percentages in mole percent: 41.6% silica (SiO₂), 29.3% calcium (CaO), 12.5% alumina (Al₂O₃), 9.1% magnesium (MgO), 6.0% iron oxide (FeO), and 1.5% nickel oxide (NiO). It will be appreciated that the nominal CMAS composition given in this definition represents a reference composition to define a benchmark for the a substance’s CMAS reactivity in a way that can be compared to the CMAS reactivity of other substances; use of this reference composition does not limit in any way the actual composition of ingested material that becomes deposited on the coating during operation which, of course, will vary widely in service.

If a given substance is capable of reacting with molten CMAS having the above nominal composition, thereby forming a reaction product that has a melting point higher than about 1200 degrees Celsius, is crystalline, and is outside the crystallization field of this nominal CMAS composition, then the substance may be useful in the protective agent as described herein. A material is outside the crystallization field of the nominal CMAS composition if it is not included in the set of crystalline phases that can be formed from combinations of the component oxides of the CMAS composition. Thus, a material that includes a rare-earth element, such as ytterbium, for instance, would be outside the crystallization field of the nominal CMAS composition because none of the component oxides of the nominal CMAS includes ytterbium. On the other hand, a reactive agent that exclusively employs one or more of the other components of the nominal CMAS composition, such as aluminum oxide, would not form a product outside the crystallization field of nominal CMAS. Use of a protective agent substance that promotes formation of reaction product with CMAS outside the crystallization field of the CMAS may result in faster reaction kinetics with CMAS under some circumstances, and if reaction kinetics can be accelerated, then ingress of molten CMAS prior to reaction and solidification desirably may be reduced.

Referring to Figure 1, an article 100 in accordance with one embodiment of the present invention includes a coating 110 disposed on a substrate 120. The coating 110 includes surface-connected voids 130 such as cracks and porosity that allow access for environmental contaminants to the exterior of coating 110. Typically the voids 130 of highest
In some embodiments, the thermal barrier coating material may further include an additional metal oxide, such as, titania, neodymia, praseodymia, urania, and hafnia, to further reduce thermal conductivity of the thermal barrier coating material.

In certain embodiments, coating 110 includes yttria-stabilized zirconia. Suitable yttria-stabilized zirconia may include from about 1 weight percent to about 20 weight percent yttria (based on the combined weight of yttria and zirconia), and more typically from about 3 weight percent to about 10 weight percent yttria. An example yttria-stabilized zirconia thermal barrier coating includes about 7% yttria and about 93% zirconia. These types of zirconia may further include one or more of a second metal (e.g., a lanthanide or actinide) oxide, such as dysprosia, erbia, europia, gadolinia, zirconia thermal barrier coating includes about 7% yttria and about 93% zirconia. These types of zirconia may further include from about 1 weight percent to about 20 weight percent yttria (based on the combined weight of yttria and zirconia), and more typically from about 3 weight percent to about 10 weight percent yttria. An example yttria-stabilized zirconia thermal barrier coating includes about 7% yttria and about 93% zirconia. These types of zirconia may further include one or more of a second metal (e.g., a lanthanide or actinide) oxide, such as dysprosia, erbia, europia, gadolinia, neodymia, praseodymia, urania, and hafnia, to further reduce thermal conductivity of the thermal barrier coatings during thermal cycling. Further, the porous structure may provide for stress reduction due to the differences between the coefficient of thermal expansion (CTE) of the coating and the CTE of the underlying bond coat layer/substrate.

An optional bondcoat 140 is disposed between coating 110 and substrate 120 in some embodiments. Bondcoat 140 provides functionality-adhesion promotion and oxidation resistance, for example-similar to what such coatings generally provide in conventional applications. In some embodiments, bondcoat 140 comprises an aluminide, such as nickel aluminate or platinum aluminate, or a MCrAlY-type coating well known in the art. These bondcoats may be especially useful when applied to a metallic substrate 120, such as a superalloy. In other embodiments, bondcoat 140 comprises a silicide compound or elemental silicon, which are often associated with ceramic-based substrates, such as silicon carbide-reinforced silicon carbide ceramic matrix composites (CMC’s). These coatings 140 may be applied using any of various coating techniques known in the art, such as plasma spray, thermal spray, chemical vapor deposition, or physical vapor deposition.

Article 100 may be any component that is subject to service in a high-temperature environment, such as a component of a gas turbine assembly. Examples of such components include, but are not limited to, components that include turbine airfoils such as blades and vanes, and combustion components such as liners and transition pieces. Substrate 120, then, may be any material suitable for use in such applications; examples include nickel-base superalloys, cobalt-base superalloys, and ceramic matrix composites, to name a few.

Coating 110 generally includes a ceramic thermal barrier material. Suitable ceramic thermal barrier coating materials include various types of oxides, such as hafnium oxide ("hafnia") or zirconium oxide ("zirconia"), in particular stabilized hafnia or stabilized zirconia, and blends including one or both of these. Examples of stabilized zirconia include without limitation yttria-stabilized zirconia, ceria-stabilized zirconia, calcia-stabilized zirconia, scandia-stabilized zirconia, magnesia-stabilized zirconia, india-stabilized zirconia, ytterbia-stabilized zirconia, lanthana-stabilized zirconia, gadolinia-stabilized zirconia, as well as mixtures of such stabilized zirconia. Similar stabilized hafnia compositions are known in the art and suitable for use in embodiments described herein.

In certain embodiments, coating 110 includes yttria-stabilized zirconia. Suitable yttria-stabilized zirconia may include from about 1 weight percent to about 20 weight percent yttria (based on the combined weight of yttria and zirconia), and more typically from about 3 weight percent to about 10 weight percent yttria. An example yttria-stabilized zirconia thermal barrier coating includes about 7% yttria and about 93% zirconia. These types of zirconia may further include one or more of a second metal (e.g., a lanthanide or actinide) oxide, such as dysprosia, erbia, europia, gadolinia, neodymia, praseodymia, urania, and hafnia, to further reduce thermal conductivity of the thermal barrier coating material. In some embodiments, the thermal barrier coating material may further include an additional metal oxide, such as, titania.

Suitable ceramic thermal barrier coating materials may also include pyrochlores of general formula $A_2B_2O_7$ where $A$ is a metal having a valence of 3+ or 2+ (e.g., gadolinium, aluminum, cerium, lanthanum or yttrium) and $B$ is a metal having a valence of 4+ or 5+ (e.g., hafnium, titanium, cerium or zirconium) where the sum of the $A$ and $B$ valences is 7. Representative materials of this type include gadolinium zirconate, lanthanum titanate, lanthanum zirconate, yttrium zirconate, lanthanum hafnate, cerium hafnate, and lanthanum cerate.

Coating 110 may include the ceramic thermal barrier coating material in an amount of up to 100 weight percent. In some embodiments, the coating 110 includes the ceramic thermal barrier coating material in a range from about 95 weight percent to about 100 weight percent and more particularly from about 98 weight percent to about 100 weight percent. The selected composition of coating 110 may depend upon one or factors, including the composition of the optional, adjacent bondcoat layer 140 (if present), the coefficient of thermal expansion (CTE) characteristics desired for coating 110, and the thermal barrier properties desired for coating 110.

The thickness of coating 110 may depend upon the substrate or the component it is deposited on. In some embodiments, coating 110 has a thickness in a range of from about 25 microns to about 2000 microns. In some embodiments, coating 110 has a thickness in a range of from about 25 microns to about 1500 microns. In some embodiments,
the thickness is in a range of from about 25 microns to about 1000 microns.

Referring again to Figure 1, a protective agent 150 is disposed within at least some of the voids 130 of coating 110. Protective agent 150 has the characteristics described above with respect to the reactivity of its component substance(s) with CMAS. In some embodiments, such as the illustrative embodiment shown in Figure 1, agent 150 decorates the surface of voids 130 in a discrete arrangement, while in other embodiments agent forms a continuous or substantially continuous structure within voids 130. While other techniques have been described in which material is disposed on internal surfaces of ceramic coatings, for instance to prevent sintering of columnar microstructural features, the present technique involves the disposition of an effective concentration of agent 150 to substantially prevent incursion of CMAS, such as the nominal CMAS composition used as a benchmark, above, into voids in which agent 150 is disposed. This effective concentration of protective agent 150 will depend in large part on the specific volume of the reaction product formed between CMAS and the agent 150, and on the microstructure of coating 110. For instance, where the width of voids 130 is comparatively large, or where the volume fraction of voids is comparatively high, the amount of agent 150 needed to be effective in stopping incursion of molten CMAS will be higher than in instances where void width and/or void volume fraction is comparatively low. In certain embodiments, at least about 25% by volume of the void fraction (porosity) of coating 110 is occupied by agent 150. In some embodiments, the volume fraction of the porosity that is occupied by agent 150 is a function of the cross-sectional depth, with a comparatively higher concentrations of agent at or near the coating surface trending to comparatively low concentrations as distance from the coating surface increases (that is, as distance away from substrate 120 decreases). For instance, as an illustrative, non-limiting example, the occupied porosity is at least about 25% by volume at the surface of coating 110, trending toward about 5% by volume at a point below the half-thickness of the coating 110.

As noted previously, protective agent 150 includes one or more substance that is highly reactive with liquid CMAS, and forms a reaction product that can serve as a barrier to prevent further incursion of liquid CMAS into voids 130, thereby helping to maintain strain tolerance of coating 110. Typically, though not necessarily exclusively, protective agent comprises a ceramic material such as an oxide or a nitride. Various types of suitable oxides are described in more detail, below. Examples of suitable nitrides include, but are not limited to, nitrides of tantalum or titanium.

In some embodiments, the protective agent includes a rare-earth oxide, that is, an oxide compound that includes a rare-earth element as one of its constituent elements.

As used herein, the terms "rare-earth" and "rare-earth element" are used interchangeably, and encompass elements of the lanthanide series, yttrium, and scandium. For example, in some embodiments, the oxide includes lanthanum, neodymium, erbium, cerium, gadolinium, or combinations including any one or more of these. Certain complex oxides, that is, oxide compounds that include more than one metal element constituent, have been shown in some circumstances to provide comparatively high reactivity with liquid CMAS. In particular embodiments, the oxide is a complex oxide that includes a rare-earth element and a transition metal element, such as zirconium, hafnium, titanium, or niobium, along with combinations of these. Zirconates, hafnates, titanates, and niobates that include lanthanum, neodymium, cerium, and/or gadolinium are examples of such complex oxide. A particular example is gadolinium zirconate, which has been shown, for example, by Kramer, Yang, and Levi at University of California, Santa Barbara, to react with liquid CMAS to form a stable crystalline apatite phase that may serve as a barrier to liquid CMAS incursion, prompting the authors to suggest this material may be useful as a bulk coating material.

Other complex rare-earth compound structures may be useful as a CMAS-reactive substance in the protective agent 150 as described herein. In one embodiment, the substance has a weberite crystal structure. Use of such materials as CMAS-resistant coatings is described in commonly-owned US Patent Application No. 14/525,586, filed on 28 October 2014. The weberite structure is an anion-deficient fluoride-related superstructure. Compared with fluorites, the reduction in the number of anions leads to a decrease in the coordination number of the so-called “B cations” (those of VI coordination) with respect to the “A cations” (VIII coordination), thus allowing the accommodation of diverse cations. The term "weberite crystal structure" as used herein refers to crystal structure of a family of materials with the general formulation A₂B₂X₇ or A₃BX₇, wherein A includes a rare earth metal ion, B includes tantalum (Ta) and/or niobium (Nb), and X comprises oxygen or fluorine. Further details of the structure have been described in "Complex Ceramic Structures I Weberites", Cai et al., Acta Crystallographica. Part B, Vol. 63, Part 3, 2009. While several other compounds possess the same stoichiometry (pyrochlores, layered perovskites etc.), the weberite compounds are isomorphous to the fluoride mineral Na₂MgAlF₇.

In some embodiments, the substance having a weberite structure comprises a rare-earth element, oxygen, and one or more element selected from the group consisting of tantalum and niobium. In particular embodiments, the substance has a nominal formula A₂BX₇, wherein A comprises a rare earth metal element, B comprises tantalum, niobium, or combinations thereof, and X comprises oxygen, fluorine, or combinations thereof. In one example, the substance having a weberite crystal structure includes gadolinium, oxygen, and at least one element selected from the group consisting of tantalum and niobium. As described in the aforementioned patent application, two different weberite oxide (Gd₃NbO₇ and Gd₃TaO₇) powder compositions were observed to react quickly and completely with liquid CMAS to form a reaction product having a desirably stable apatite-type structure with a nominal composition Ca₂Gd₆(SiO₄)₆O₂.
In other embodiments, the protective agent comprises a NZP type material, as described in commonly owned US Patent Application No. 14/524,072, filed on 27 October 2014. The term "NZP-type material" as used herein refers to a family of materials having a crystal structure similar to NaZr₂P₃O₁₂ (the parent compound from which the name is derived). The NZP materials typically have a three-dimensional "open" framework structure, with ZrO₆ octahedra linked to PO₄ tetrahedra. In some embodiments, the NZP-type material has a hexagonal structure. As for the other materials described above, NZP-type materials have been described previously as candidates for bulk coatings. In the present description, however, these materials are disposed in the voids 130 of a bulk coating 110.

In one embodiment employing NZP-type material as a substance of the protective agent 150, the substance is a material having formula (I):

\[ A_{1-x}B_xZr_{4+y}D_y(PO_4)_z \]

wherein A and B are selected from the group consisting of alkaline earth metals and rare earth metals, D is hafnium or titanium; x is a number from 0 to 1; y is a number from 0 to 4; and z is 3 or 6. Non-limiting examples of suitable alkaline earth metals include beryllium, magnesium, calcium, strontium, barium, or combinations thereof. Non-limiting examples of suitable rare earth metals include scandium, yttrium, lanthanum, cerium, gadolinium, praseodymium, neodymium, promethium, samarium, europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, or combinations thereof.

In certain embodiments, the CMAS-reactive material includes CaₓSr₁₋ₓZr₄(PO₄)₆, wherein x is a number from 0 to 1. In certain embodiments, the CMAS-reactive material includes CaZr₄(PO₄)₆, SrZr₄(PO₄)₆, Ca₀.₅Sr₀.₅Zr₄(PO₄)₆, or combinations thereof. In these compositions, rare-earth elements are included in the protective agent 150 in many of the various embodiments. While several compounds including these elements may show desirable reactivity with CMAS, there may be certain deleterious effects attributable to the presence of these elements within coating 110. Notably, the present inventors have discovered that where protective agent 150 is disposed at or near the interface between coating 110 and bondcoat 140, chemical interaction between the rare-earth-bearing protective agent and an oxide formed by the bondcoat at elevated temperature-known as a thermally-grown oxide, or TGO-can result in premature spalling of coating 110.

To mitigate this potential issue, some embodiments of the present invention employ a barrier agent 160 disposed to substantially separate protective agent 150 from bondcoat 140 or, if no bondcoat is present, from substrate 120. Thus the barrier agent 160 is interposed between substrate 120 and protective agent 150. Barrier agent 160 substantially prevents chemical interaction between protective agent 150 and a TGO disposed on substrate 120 or, if present, bondcoat 140. In some embodiments, barrier agent 160 comprises aluminum oxide, cerium oxide, yttrium oxide, zirconium oxide, hafnium oxide, tantalum oxide, niobium oxide, titanium oxide, or combinations thereof. Some of these oxides may, where appropriate, include a sufficient amount of stabilizer (often a rare earth element) to reduce propensity of the oxide to undergo stress-generating phase transformations during heat-up and cool-down, but the amount of rare-earth stabilizer should be sufficiently small to mitigate issues of reactivity with the aforementioned TGO. The upper limit of rare-earth stabilizer content depends on the particular element being used and the identity of the barrier agent 160; for example, rare earth bearing aluminate garnets tend not to dissolve alumina, and thus may contain higher amounts of rare earth material without deleterious interaction with TGO. In some embodiments, barrier agent 160 comprises less than about
Coating 110 is shown in Figure 1 as a single layer, but in some embodiments, such as that illustrated in Figure 2, coating 110 comprises a plurality of layers 220. In the embodiment illustrated in Figure 2, coating 110 includes a first layer 222, comprising a first material, and a second layer 224 comprising a second material. First layer 222 is disposed between second layer 224 and substrate 120. The second material is resistant to CMAS infiltration. A material is considered "resistant to CMAS infiltration" in this context if it is more resistant, relative to 8 mole percent yttria stabilized zirconia ("8YSZ" as noted above), to infiltration by liquid CMAS having the nominal CMAS composition described previously herein at a temperature of 1300 degrees Celsius. Similarly to what has been noted previously, it will be appreciated that the 1300 degree Celsius temperature and the nominal CMAS composition given in this definition represent a reference temperature and a reference composition to define a benchmark for the material's CMAS resistance in a way that can be compared to the CMAS resistance of 8YSZ; use of these reference values does not limit in any way the actual temperature at which article 100 may operate or the actual composition of ingested material that becomes deposited on the coating during operation, both of which, of course, will vary widely in service.

Many different materials have been described in the art as providing enhanced CMAS protection relative to yttria-stabilized zirconia and other standard TBC materials, and any of these materials may be considered for use in second layer 224 described above. In one embodiment, the second material includes an oxide. Oxides that include one or more transition metal elements, rare-earth elements, silicon, and/or indium have been described in the art as being resistant to CMAS. In one embodiment, the oxide includes zirconium, hafnium, titanium, or combinations thereof. Zirconia, hafnia, and/or titania materials stabilized with one or more rare-earth elements have been described in the art of CMAS-resistant coatings.

Examples of such materials include coatings containing gadolinia and zirconia, such as gadolinia-stabilized zirconia; and coatings containing mixtures of gadolinia and hafnia. Examples of other potentially suitable oxide materials include pyrochlores, such as lanthanum zirconate; garnets, such as those described in US Patent Number 7,722,959; and oxyapatites, such as those described in US Patent Number 7,722,959. Sodium-containing oxides, such as sodium oxide, sodium silicate, and sodium titanate, are other examples of CMAS resistant oxide materials.

In one particular example, the second material includes yttria-stabilized zirconia (YSZ) having higher yttria content (relative to the overall YSZ content) than typical 8YSZ. Generally, the yttria content in this example is greater than 38 weight percent, and in specific embodiments the yttria content is at least about 55 weight percent. Coatings as described herein using YSZ with yttria content greater than 38 weight percent were superior in CMAS resistance to coatings made with lower-yttria YSZ materials.

Other materials besides oxides have been described for use in resisting CMAS, and are also considered as potentially useful as second materials in second layer 224. Examples of such alternative materials include carbides (such as silicon carbide, tantalum carbide, titanium carbide, and others), nitrides (such as silicon nitride, zirconium nitride, tantalum nitride, boron nitride, and others), and silicides (such as chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, and others).

Protective agent 150 is distributed within surface-connected coating voids 130 as described previously, and in the context of embodiments involving multiple layers 220 (Figure 2), the protective agent 150 is, in some embodiments, disposed in just a portion of the layers 220, such as in second layer 224 only, or first layer 222 only; while in certain embodiments, such as the example illustrated in Figure 2, protective agent 150 is disposed in all layers 220. Barrier agent 160 similarly may be disposed in one or more layers 220; in embodiments such as that illustrated in Figure 2, barrier agent 160 is disposed in first layer 222 to protect bondcoat 140 and/or substrate 120 from interaction with protective agent 150.

One potential advantage of the technique described herein is that it allows the use of an outermost layer, such as layer 222, that has desirable wear, erosion, thermal, or other properties, while disposing CMAS resistant material (i.e., protective agent 150) in the places where it is most needed. Many of the materials that are highly reactive with CMAS lack suitable levels of mechanical properties or other properties to be desirable choices for a bulk coating that is exposed to the ambient service environment of, for instance, a gas turbine. On the other hand, zirconia stabilized with 7%-9% yttria by weight is a very attractive material for use in thermal barrier coatings because of its advantageous thermal and mechanical properties, but its resistance to CMAS is not particularly high. The life of such a coating material may be enhanced by applying protective agent 150 to vulnerable areas (such as the surface-connected voids 130 as noted herein) without resorting to the use of a bulk topcoat made of a CMAS-resistant material, which may itself be more vulnerable than YSZ to erosion or other degradation mechanism.

A method for making articles such as article 100 includes disposing protective agent 150 within surface connected voids 130 of coating 110 at an effective concentration to substantially prevent incursion of CMAS materials, such as nominal CMAS noted above, into voids 130 in which agent 150 is disposed.
As noted previously, coating 110 may be disposed on substrate 120 by any of several different coating techniques, such as plasma spray techniques (for example, air plasma spray using dry or liquid feedstock materials), chemical vapor deposition, physical vapor deposition (for example, electron-beam physical vapor deposition or evaporation), slurry deposition, sol-gel techniques, and other coating methods.

Disposing protective agent typically involves infiltrating an existing coating 110 with a vapor or liquid into the surface-connected voids 130 of the coating 110. In the case of a vapor infiltrant, protective agent 150 may be formed by chemical interaction with the environment within voids 130 such as by reaction with material of coating 110. Liquid infiltrants, on the other hand, include one or more liquids such as water, or a carbon-bearing liquid such as an alcohol or acetone. In one embodiment involving a liquid infiltrant, the liquid includes a carrier fluid and a plurality of particles suspended within the carrier fluid. The particles may comprise the protective agent 150 composition, or may be a chemical precursor to this composition, designed to further react during processing or during service to produce protective agent 150. In an alternative embodiment, the liquid includes a solvent, with a solute dissolved in the solvent. The solute may be a precursor of protective agent 150, such as a nitrate, sulfate, other salt, or other compound type, and the solvent is selected to appropriately accommodate the desired solute. More than one solute may be dissolved in the solvent. The solute may be reacted to form agent 150, such as by heating to decompose the solute, or by reacting multiple solutes together, or by reacting one or more solute with the material of coating 110, or some combination of these.

The liquid infiltrant is infiltrated into the surface-connected voids 130 using any appropriate technique. In some embodiments, the liquid is simply placed in contact with coating 110, such as by dipping or brushing, allowing capillary action to draw the liquid and agent 150 (or precursor thereof) into the voids 130. Vacuum infiltration techniques are applied in some embodiments to further assist in driving liquid into coating 110. Other techniques such as electrophoretic deposition may be used in conjunction with a suspension to deposit particles of agent or a precursor of agent 150 into voids 130. Use of electrophoretic deposition to deposit material within the voids of a ceramic coating is described by Hasz in US Patent number 7,780,832.

Where a liquid infiltrant is applied, whether the liquid is carrying a suspension of particles or has a solute dissolved in it, in some embodiments the method further includes volatilizing the liquid to form a residue that is disposed in voids 130. The residue may be a precursor to agent 150, or it may be the agent composition itself. Volatilizing is typically done by heating the infiltrated coating to a temperature where the liquid is driven off at an acceptable rate. Often the heating rate ("ramp-rate") to attain the desired temperature for volatilization is controlled to avoid building up undue pressure within the coating, which could damage the coating and/or could result in incomplete deposition of protective agent due to liquid being forced out by rapid bubble formation and escape.

In some embodiments, the method further includes interposing barrier agent 160 between protective agent 150 and substrate 120, for instance by disposing barrier agent 150 within pores 130 where bondcoat 140 and coating 110 meet. This disposition of barrier agent may be accomplished by any means, such as those described above for disposing protective agent 150. In some embodiments, a suspension of particles comprising the desired barrier agent composition, such as aluminum oxide, cerium oxide, zirconium oxide, hafnium oxide, tantalum oxide, niobium oxide, titanium oxide, or combinations thereof, is infiltrated into the voids 130 of coating. The liquid portion of this suspension is volatilized, and then the protective agent is disposed as described above. In alternative embodiments, a liquid solution of a precursor of the barrier agent is infiltrated into coating 110, the liquid is driven off, leaving a residue within the voids 130 that is later reacted to form the barrier agent. This reaction can occur prior to, during, or after disposition of the protective agent, depending on the desired processing and materials distribution.

Other techniques may be applied to provide barrier agent 160 or to otherwise protect substrate 120 or bondcoat 140 from interacting with protective agent 150. In one embodiment, an initial layer of coating 110 is applied, such as by electron-beam physical vapor deposition (EBPVD). This initial layer is infiltrated as described above to deposit barrier agent 160 within voids (such as between columns) of this initial layer of coating 110. The infiltrated layer is then cleaned and coated with a subsequent layer of coating 110. This subsequent layer may be the same material as used in the initial layer, or may be a different material, as noted above for the structure described in Figure 2. The subsequent layer is then infiltrated and processed to dispose protective agent 150 within its voids 130. In another embodiment, an initial layer of coating is deposited using a deposition technique that provides a comparatively high density coating. This dense initial layer may have sufficient density to serve as a barrier between protective agent 150 and substrate 120 or bondcoat 140. A subsequent technique or change in deposition parameters may then be applied to deposit a subsequent layer of comparatively porous material over the initial comparatively dense layer. This subsequent layer is then subjected to infiltration and further processing to dispose protective agent 150 within its voids 130.

EXAMPLES

The following examples are presented to further illustrate non-limiting embodiments of the present invention.

Gadolinium nitrate hexahydrate and zirconium dinitrate oxide hydrate were dissolved in ethanol to form 1M solutions of the metal ion at room temperature (20°C). The solutions were mixed in a 1:1 volume ratio to form a precursor
solution (precursor to protective agent 150) when disposed into the coating 110. The coating 110 on a substrate 120 was submersed under a vacuum (about 558 Torr) into the solution for three minutes in a bell jar. The bell jar was returned to room air pressure and the substrate 120 with the coating 110 infiltrated with the precursor protective agent 150 was removed from the precursor solution. The substrate with the coating was heated to 80°C for thirty minutes (to dry the ethanol) and put into a furnace at 700°C for thirty minutes to decompose the nitrate salts in the coating 110 and convert to Gd$_2$Zr$_2$O$_7$ protective agent 150. These steps were repeated up to 25 times to obtain a weight gain of protective agent 150 in the coating 110 of about 4-15 mg/cm$^2$.

[0052] In another example, gadolinium nitrate hexahydrate and zirconium dinitrate oxide hydrate were dissolved in ethanol to form 1M solutions of the metal ion at room temperature (20°C). The solutions were mixed in a 1:1 volume ratio to form a precursor solution (precursor to protective agent 150) when disposed into the coating 110. The precursor solution was brushed onto the surface of the coating 110 on a substrate 120 using a nylon brush, wetting the surface of the coating 110. The substrate with the coating was heated to 80°C for thirty minutes (to dry the ethanol) and heated in a furnace at 300°C for thirty minutes to decompose the nitrate salts in the coating 110. This process of brushing the solution on the coating and heating at 80°C followed by 300°C was repeated 5 times, and followed by a heat treatment at 700°C for thirty minutes to convert the nitrate precursors to Gd$_2$Zr$_2$O$_7$ protective agent 150. The surface of the coating 110 was brushed after heat treatment to remove loose oxide powder to increase the effectiveness of further infiltrations. The process was repeated until in total the coating was brushed 25 times with the nitrate salt solutions, with 5 excursions to 700°C, resulting in a weight gain of protective agent 150 in the coating 110 of about 4-15 mg/cm$^2$.

[0053] In another example, a barrier agent 160 was applied to the coating 110 at the interface between bond coat 140 and coating 110 before the protective agent 150 was applied. Aluminum nitrate nonahydrate was dissolved in water to form a 1M solution at room temperature (20°C). The solution was stabilized with citric acid and pH adjusted to pH ∼6 with ammonium hydroxide (NH$_4$OH). The coating 110 on a substrate 120 was submersed under a vacuum (558 Torr) into the solution for three minutes in a bell jar. The bell jar was returned to room air pressure and the substrate 120 with the coating 110 infiltrated with the precursor barrier agent 160 was removed from the precursor solution. The substrate with the coating was heated to 80°C for thirty minutes (to dry the ethanol) and put into a furnace at 700°C for thirty minutes to decompose the precursor barrier agent to an oxide at the coating 110 - bond coat 140 interface and convert to alumina (Al$_2$O$_3$) barrier agent 160. These steps were repeated up to 5 times to obtain a weight gain of barrier agent 160 in the coating 110 of about 1-5 mg/cm$^2$. After the barrier agent is applied, the protective agent 150 can be applied to the coating 110 on the substrate 120 in accordance with the techniques described herein.

[0054] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the true spirit of the invention.

[0055] Various aspects and embodiments of the present invention are defined by the following numbered clauses:

1. An article comprising:
   - a coating disposed on a substrate, the coating comprising a plurality of elongated surface-connected voids; and
   - a protective agent disposed within at least some of the voids of the coating;
   - wherein the protective agent comprises a substance capable of chemically reacting with liquid nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS,
   - wherein the solid crystalline product has a melting temperature greater than about 1200 degrees Celsius.

2. The article of clause 1, wherein the protective agent is present in the coating in an effective concentration to substantially prevent incursion by said nominal CMAS into voids in which the protective agent is disposed.

3. The article of clause 1 or clause 2, wherein the protective agent comprises a nitride, an oxide, or combinations thereof.

4. The article of any preceding clause, wherein the protective agent comprises a rare earth oxide.

5. The article of any preceding clause, wherein the oxide comprises lanthanum, neodymium, erbium, cerium, or gadolinium.

6. The article of any preceding clause, wherein the oxide further comprises zirconium, hafnium, titanium, tantalum, or niobium.
7. The article of any preceding clause, wherein the substance has a weberite crystal structure.

8. The article of any preceding clause, wherein the substance comprises a rare-earth element, oxygen, and an element selected from the group consisting of tantalum and niobium.

9. The article of any preceding clause, wherein the substance has a nominal formula $A_{3}BX_{7}$, wherein A comprises a rare earth metal element, B comprises tantalum, niobium, or combinations thereof, and X comprises oxygen, fluorine, or combinations thereof.

10. The article of any preceding clause, wherein the substance has a weberite crystal structure and comprises gadolinium, oxygen, and at least one element selected from the group consisting of tantalum and niobium.

11. The article of any preceding clause, wherein the protective agent comprises an oxide having the nominal formula $A_{1-x}B_xZr_{4-y}D_y(PO_4)_z$; wherein A and B are selected from the group consisting of alkaline earth metals and rare earth metals, D is hafnium or titanium, $x$ is a number from 0 to 1; $y$ is a number from 0 to 4; and $z$ is 3 or 6.

12. The article of any preceding clause, wherein the protective agent comprises $MZr_4(PO_4)_6$, wherein M comprises at least one alkaline earth metal.

13. The article of any preceding clause, wherein the protective agent comprises $CaxSr_{1-x}Zr_4(PO_4)_6$, wherein x is a number from 0 to 1.

14. The article of any preceding clause, wherein the protective agent comprises $CaZr_4(PO_4)_6$, $SrZr_4(PO_4)_6$, $Ca_{0.5}Sr_{0.5}Zr_4(PO_4)_6$, or combinations thereof.

15. The article of any preceding clause, wherein the substance has a perovskite crystal structure and comprises (a) a rare earth element, (b) tantalum, niobium, or a combination of tantalum and niobium, and (c) oxygen.

16. The article of any preceding clause, wherein the substance comprises gadolinium, tantalum, and oxygen.

17. The article of any preceding clause, wherein the substance comprises a compound having a scheelite, fergusonite, or wolframite crystal structure, and having a nominal formula $ABX_4$, wherein A comprises a rare-earth element, B comprises tantalum, niobium, or a combination of tantalum and niobium, and X comprises oxygen, nitrogen, or a combination of nitrogen and oxygen.

18. The article of any preceding clause, wherein A comprises yttrium, gadolinium, lanthanum, neodymium, ytterbium, or combinations of any of the foregoing.

19. The article of any preceding clause, wherein the coating comprises a plurality of layers.

20. The article of any preceding clause, wherein the coating comprises a first layer comprising a first material and a second layer comprising a second material, the first layer disposed between the second layer and the substrate, wherein the second material is more resistant to infiltration by nominal CMAS relative to 8 weight percent yttria-stabilized zirconia at a temperature of 1300 degrees Celsius.

21. The article of any preceding clause, wherein the second material comprises yttria-stabilized zirconia, with a yttria content greater than about 38 weight percent.

22. The article of any preceding clause, wherein the yttria content is at least about 55 weight percent.

23. The article of any preceding clause, wherein second material comprises at least one transition metal element, at least one rare-earth metal element, silicon, indium, or combinations thereof.

24. The article of any preceding clause, further comprising a barrier agent interposed between the substrate and the protective agent.

25. The article of any preceding clause, wherein the barrier agent comprises less than 34 atomic per cent rare earth...
26. A method, comprising:

disposing a protective agent within a plurality of elongated surface-connected voids of a coating;

wherein the protective agent comprises a substance capable of chemically reacting with nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS,

wherein the solid crystalline product has a melting temperature greater than about 1200 degrees Celsius, and

wherein the protective agent is present in the coating in an effective concentration to substantially prevent incursion by said nominal CMAS into voids in which the protective agent is disposed.

27. The method of any preceding clause, wherein disposing comprises infiltrating the voids with a liquid.

28. The method of any preceding clause, wherein the liquid comprises a carrier fluid and a plurality of particles suspended within the carrier fluid.

29. The method of any preceding clause, wherein the liquid comprises a solvent and a solute dissolved in the solvent.

30. The method of any preceding clause, wherein the solute comprises a precursor of the substance.

31. The method of any preceding clause, further comprising reacting the precursor to form the substance.

32. The method of any preceding clause, further comprising volatilizing the liquid to form a residue disposed in the voids.

33. The method of any preceding clause, further comprising interposing a barrier agent between the protective agent and a substrate upon which the coating resides.

Claims

1. An article (100) comprising:

   a coating (110) disposed on a substrate (120), the coating (110) comprising a plurality of elongated surface-connected voids (130); and

   a protective agent (150) disposed within at least some of the voids (130) of the coating (110);

   wherein the protective agent (150) comprises a substance capable of chemically reacting with liquid nominal CMAS to form a solid crystalline product outside the crystallization field of said nominal CMAS,

   wherein the solid crystalline product has a melting temperature greater than about 1200 degrees Celsius.

2. The article (100) of claim 1, wherein the protective agent (150) is present in the coating (110) in an effective concentration to substantially prevent incursion by said nominal CMAS into voids (130) in which the protective agent (150) is disposed.

3. The article (100) of claim 1 or claim 2, wherein the protective agent (150) comprises a nitride, an oxide, or combinations thereof.

4. The article (100) of any preceding claim, wherein the protective agent (150) comprises a rare earth oxide.

5. The article (100) of any preceding claim, wherein the substance has a weberite crystal structure.

6. The article (100) of any preceding claim, wherein the substance comprises a rare-earth element, oxygen, and an element selected from the group consisting of tantalum and niobium.

7. The article (100) of any preceding claim, wherein the protective agent (150) comprises an oxide having the nominal elements.
formula $A_{1-x}B_xZr_4-yD_y(PO_4)_z$.
wherein A and B are selected from the group consisting of alkaline earth metals and rare earth metals, D is hafnium or titanium, x is a number from 0 to 1; y is a number from 0 to 4; and z is 3 or 6.

8. The article (100) of any preceding claim, wherein the protective agent (150) comprises MZr₄(PO₄)₆, wherein M comprises at least one alkaline earth metal.

9. The article (100) of any preceding claim, wherein the substance has a perovskite crystal structure and comprises (a) a rare earth element, (b) tantalum, niobium, or a combination of tantalum and niobium, and (c) oxygen.

10. The article (100) of any preceding claim, wherein the substance comprises gadolinium, tantalum, and oxygen.

11. The article (100) of any preceding claim, wherein the substance comprises a compound having a scheelite, fergusonite, or wolframite crystal structure, and having a nominal formula $ABX_4$, wherein A comprises a rare-earth element, B comprises tantalum, niobium, or a combination of tantalum and niobium, and X comprises oxygen, nitrogen, or a combination of nitrogen and oxygen.

12. The article (100) of any preceding claim, wherein A comprises yttrium, gadolinium, lanthanum, neodymium, ytterbium, or combinations of any of the foregoing.

13. The article (100) of any preceding claim, wherein the coating (110) comprises a plurality of layers (220).

14. The article (100) of any preceding claim, further comprising a barrier agent (160) interposed between the substrate (120) and the protective agent (150).

15. The article (100) of claim 14, wherein the barrier agent (160) comprises less than 34 atomic per cent rare earth elements.
## DOCUMENTS CONSIDERED TO BE RELEVANT

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