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(71) Applicant: **UNITED TECHNOLOGIES CORPORATION** [US/US]; One Financial Plaza, Hartford, Connecticut 06103 (US).

(72) Inventors: **LITTON, David A.**; 22 Hilltop Drive, West Hartford, Connecticut 06107 (US). **TRYON, Brian S.**; 1828 Main Street, Apt. #1, Glastonbury, Connecticut 06033 (US).

(74) Agent: **SLATE, William B.**; BACHMAN & LAPOINTE, P.C., c/o CPA Global, P.O. Box 52050, Minneapolis, Minnesota 55402 (US).

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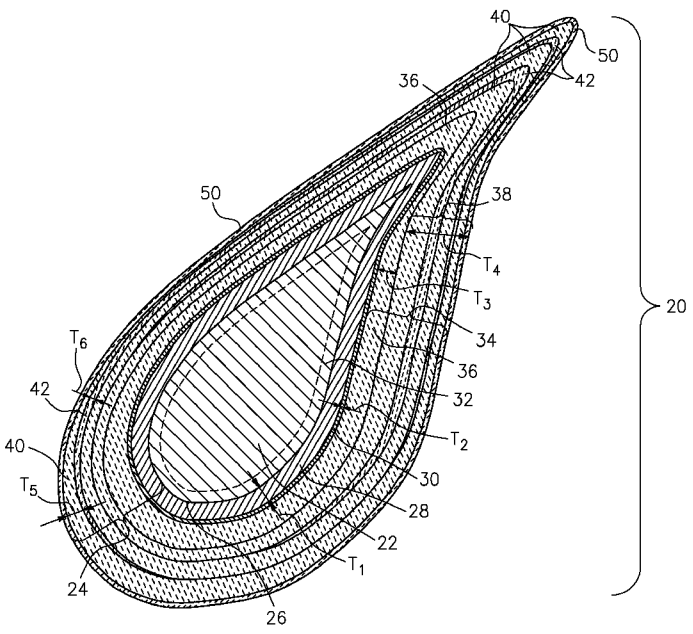

FIG. 1

(57) Abstract: The thermal barrier coating system comprises a matrix (40) of a first chemistry with multiple embedded second phases (42) of a second chemistry. The matrix comprises a stabilized zirconia. The second regions comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof. The second phases have a characteristic thickness (T_6) of less than 2.0 micrometers (μm). The spacing between second phases has a characteristic thickness (T_5) of less than 8.0 micrometers (μm).

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MULTI-MATERIAL THERMAL BARRIER COATING SYSTEM

BACKGROUND

The disclosure relates to thermal barrier coating systems. More particularly, the disclosure relates to thermal barrier coating systems for gas turbine.

US Patent No. 7785722 (the '722 patent) discloses a thermal barrier coating system comprising a YSZ base layer. Thereatop there may be several alternating layers of a molten silicate resistant material and YSZ. The molten silicate resistant material may comprise an oxide of a lanthanide.

SUMMARY

One aspect of the disclosure involves an article comprising a thermal barrier coating system atop a three-dimensional substrate. The thermal barrier coating system comprises a matrix of a first chemistry with multiple embedded second phases of a second chemistry. The matrix comprises a stabilized zirconia. The second regions comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof. The second phases have a characteristic thickness (T_6) of less than 2.0 micrometers (μm). The spacing between second phases has a characteristic thickness (T_5) of less than 8.0 micrometers (μm).

In additional or alternative embodiments of any of the foregoing embodiments: the matrix comprises a yttria stabilized zirconia; and the second phases comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is

selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

In additional or alternative embodiments of any of the foregoing embodiments: the second phases have characteristic thickness (T_6) of 0.15-1.0μm; and a ratio of the second phases characteristic thickness (T_6) to the spacing (T_5) between second phases, thickness-wise, is between 1:3 and 1:4.

In additional or alternative embodiments of any of the foregoing embodiments: the matrix with embedded second phases form a layer having a thickness (T_4) of at least 76 micrometers.

In additional or alternative embodiments of any of the foregoing embodiments: the matrix with embedded second phases form a layer having a thickness (T_4) of 76-350 micrometers.

In additional or alternative embodiments of any of the foregoing embodiments, the article further comprises: a bondcoat; and a first TBC layer between the bondcoat and the matrix.

In additional or alternative embodiments of any of the foregoing embodiments: the first layer has a nominal composition differing from a composition of the matrix by the presence of one or more additives in a total amount of up to 1.0 weight percent.

In additional or alternative embodiments of any of the foregoing embodiments: the characteristic thickness (T_6) of the second phases is 0.15-1.0 micrometers (μm), and the

characteristic thickness (T_5) of the spacing between second phases is 0.5-3.0 micrometers (μm).

In additional or alternative embodiments of any of the foregoing embodiments, the article further comprises: an additional coating layer with a homogeneous chemistry atop the matrix with embedded second phases.

In additional or alternative embodiments of any of the foregoing embodiments: the additional coating layer is more resistant to attack by molten silicate deposits than is the matrix.

In additional or alternative embodiments of any of the foregoing embodiments, the article further comprises: an additional coating layer atop the matrix and comprising oxyapatite and/or garnet.

In additional or alternative embodiments of any of the foregoing embodiments: the matrix and second phases are in a layer of the thermal barrier coating system with thickness (T_4) wherein the second phases account for 5-20% of said layer by volume.

Another aspect of the disclosure involves an article comprising: a substrate; and a thermal barrier coating system atop the substrate and having a matrix having a first chemistry and a plurality of embedded second phases layered within the matrix having a second chemistry, different from the first chemistry, wherein the embedded second phases within the matrix have a characteristic perimeter extent of 30-85%.

In additional or alternative embodiments of any of the foregoing embodiments: the matrix comprises a yttria

stabilized zirconia; and the second phases comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

In additional or alternative embodiments of any of the foregoing embodiments: at a given location, a depthwise number of the embedded second regions is 7-84.

Another aspect of the disclosure involves a process for coating a substrate, the process comprising: generating a plume of deposition material from a first source and a second source; alternating the composition of the plume by generating vapor from the first and second sources in an alternating manner; and moving the substrate relative to the first and second sources, wherein the moving of the substrate moves a given region of the substrate through the plume at a cyclic rate having a period greater than a duration of generation of the vapor plume from the second source.

In additional or alternative embodiments of any of the foregoing embodiments: the moving consists of a rotation.

In additional or alternative embodiments of any of the foregoing embodiments: a duration of generation of the vapor plume from the first source is 400-5000% of said period; and the duration of generation of the vapor plume from the second source is 30-99% of said period.

In additional or alternative embodiments of any of the foregoing embodiments: the first source comprises a yttria stabilized zirconia; and the second source comprises at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is

selected from the lanthanide La through Lu, Y, Sc, In, Ca, and Mg.

In additional or alternative embodiments of any of the foregoing embodiments: the first source comprises a yttria stabilized zirconia; and the second source comprises at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanide La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

In additional or alternative embodiments of any of the foregoing embodiments: the relative speed of the moving and the frequency of alternation of the composition of the vapor plume are effective to deposit a matrix with embedded second phase patches of the coating from the first source and second source, respectively.

In additional or alternative embodiments of any of the foregoing embodiments: each of the second phase patches represents less than 85% of the surface area of the substrate.

The details of one or more embodiments are set forth in the accompanying drawings and the description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional schematic view of a coated substrate with various layers of exaggerated thickness to various degrees.

FIG. 2 is a partially schematic view of a first coating system in a first deposition condition.

FIG. 3 is a view of the first coating system in a second deposition condition.

FIG. 4 is a view of the first coating system in a third deposition condition.

FIG. 5 is a view of the first coating system in a fourth deposition condition.

Like reference numbers and designations in the various drawings indicate like elements.

DETAILED DESCRIPTION

FIG. 1 schematically shows a coated part 20 comprising a metallic substrate 22 and a thermal barrier coating system 24 atop the surface 26 of the substrate. After any surface preparation of the substrate, an initial deposited layer 28 of the coating system is a bondcoat. Exemplary bondcoat is an MCrAlY, where M refers to a metal, typically Ni and/or Co. An alternate bondcoat is a diffusion aluminide. Exemplary bondcoat deposition is via low pressure plasma spray (LPPS), high velocity oxy-fuel (HVOF), air plasma spray (APS), cathodic arc deposition, plating, and the like. The bondcoat has a thickness T_1. The exemplary as-deposited bondcoat thickness may be reduced via growth of a thermally grown oxide 30 which may grow during subsequent stages of deposition and is shown having a thickness T_2. Exemplary T_1 as applied is 0.3-9 mil (7.6-229μm), more narrowly 0.5-7 mil (13-178μm). The bondcoat may also diffuse with the substrate creating a diffusion region or zone 32.

A multi-layer ceramic thermal barrier coating (TBC) 34 may be applied after bondcoat application. The exemplary TBC 34 comprises a base layer 36 applied to a thickness T_3. The exemplary base layer is 7YSZ. More broadly, it may be a YSZ such as a 3-9% yttria with balance zirconia. Exemplary T_3 is 0.1-5 mil (2.5-127μm), more narrowly, 0.5-3.5 mil (12.7-89μm).

Atop the base layer 36, the TBC 34 includes a layer 38 having a thickness T_4 and comprising a matrix 40 and embedded second phases 42. FIG. 1 is not drawn to scale. Specifically, the illustrated coating thickness is extremely exaggerated relative to the substrate size for the sake of clarity. The illustrated coating thickness variation around the part is not realistic. Also, the illustrated thicknesses of the embedded

second phases are also exaggerated for clarity. Also, the number of illustrated embedded second layers is lower than likely.

The matrix 40 has a first chemistry and the embedded second phases 42 have a second chemistry, different from the first chemistry. The bondcoat layer 28 and the base layer 36 are essentially continuous and of essentially constant thickness over the relevant area of the substrate (e.g., allowing for variations in substrate geometry and for intended differences in thicknesses (e.g., tapering toward near zero at a trailing edge of an airfoil so as to limit aerodynamic losses). Alternatively, with a combustor panel, a relatively uniform thickness along a hot side of the combustor panel but less or no thickness along a cold side of a combustor panel.

The embedded second phases 42 may form incomplete layers that do not extend all the way around the three-dimensional substrate, such that they are embedded within the matrix 40. This is shown in FIG. 1.

Exemplary characteristic thickness T_6 of the embedded second phases 42 are measured via an appropriate average (mean, medial, mode, optionally weighted by the amount of material at such thickness). Alternatively, T_6 may be a maximum measurement averaged among the regions of a given type. In general, similar thickness numbers may be used as these different definitions may be expected to account for variations of about a factor of two or less. Exemplary T_6 is 0.1-2.0μm, more narrowly, 0.15-1.0μm or 0.2-0.8μm.

Exemplary characteristic thicknesses T_5 of the matrix 40 between second phases 42 are measured via an appropriate average (mean, medial, mode, optionally weighted by the amount

of material at such thickness). Alternatively, T_5 may be a maximum measurement averaged among the regions of a given type. In general, similar thickness numbers may be used as these different definitions may be expected to account for variations of about a factor of two or less. Exemplary T_5 is 0.3-8.0μm, more narrowly, 0.5-5.0μm or 1.0-3.0μm.

Exemplary T_4 is 5-700μm, more narrowly, 20-600μm or 50-500μm.

Exemplary T_3 is 3-125μm, more narrowly, 5-100μm or 12-75μm.

As discussed below, the extent to which each individual exemplary embedded phase 42 would extend around the part in the plane of the page would depend on the proportion of a single rotation period during which deposition of the coating chemistry corresponding to that instance of embedded phase 42 was allowed. Exemplary proportions of the substrate surface area that each of the embedded phases 42 would cover would range from 30% to 99%, more narrowly, 30-85% or 50% to 85%. Thus, with variations depending on substrate geometry, viewed about an axis of rotation during coating, the embedded faces 42 would cover such percentages of the perimeter of the part (e.g., exact correspondence if cylindrical). In an alternative definition, such percent extents are measured between boundaries of the phases 42 where each such phase diminishes to 5 percent of its mean thickness.

At a given location along the coated substrate, the depthwise number of second phases 42 may be at least two, more narrowly, at least four or at least ten. Relative to the thickness T_4, the number of second phases 42 at a given depthwise location may increase with T_4. With lowest T_4 of up to 3.0 mil (76μm), an exemplary number is 1-12, more narrowly, 2-12 or 2-7. At an exemplary T_4 of 21.0 mil (533μm), the exemplary range would be

7-84, more narrowly, 14-49. Thus, the upper limits of these ranges at 3.0 and 21.0 mil may define an upper boundary of a linear function depending upon T_4 and the lower boundaries may form a lower linear limit.

There may be further variations. For example, there may be additional layers such as a topcoat 50 (discussed below). Overall, and even with such exemplary additional layers, the thickness T_4 of the layer 38 may represent at least an exemplary 30% of a total coating thickness, more narrowly, 50-90%.

In an exemplary implementation, the matrix 40 may have a conventional TBC composition such as a YSZ (e.g., 3-9 weight percent YSZ, or, in particular, 7YSZ) which may be the same as the composition of the base layer 36. Among possible candidate situations for differences between the base layer 36 and the matrix 40 is the use of a luminescent dopant in the base layer. An exemplary dopant is a lanthanide. A laser may be used to excite luminescence from the dopped layer. The luminescence is captured by fiber optics and analyzed. Resulting information can be used for health monitoring of the TBC. Among candidate lanthanides are Eu and Er (because their luminescence wavelengths are in ranges that TBCs do not absorb and the luminescent lifetimes are long enough at high temperatures to get a good signal to noise ratio). Other possible additives are Ti and/or Ta in small amounts to increase the toughness of the base layer. Although small variations between the composition of the layers 40 and the base layer 36 may be desirable from performance aspects, ease of manufacturing and using a common deposition material source may suggest using the same composition or a composition differing only in contamination from materials of the embedded second phases.

The embedded second phases 42 may consist of a material having a significantly lower mechanical strength and fracture toughness than the material of the matrix 40. Any in-plane stresses that exceed the strength of the weak phases 42 (typically 50 to 200 ksi (345-1379 MPa) or 75-150 ksi (517-1034 MPa)) or in-plane strain energy that exceeds the fracture toughness of phases 42 (typically 1-5 J/m^2) would be expected to form cracks within phases 42 that would relieve stresses and dissipate strain energy. The associated interembedding of phases 42 within the matrix 40 ensures that any cracks forming in phases 42 would be contained within those phases - thereby avoiding linking of cracks that might lead to large spalls. The fact that the thickness T_6 of phases 42 is intentionally kept small would ensure that crack would not widen as they grow, ensuring both crack bridging and friction in the crack wake (both of which would promote dissipation of any strain energy built up in the coating).

Exemplary second phase 42 material may comprise an oxide of a lanthanide or similar material (e.g., material selected from the group consisting of the lanthanides La through Lu (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Y, Sc, In, Ca, and Mg). More specifically, the second phase material may comprise a combination of such oxide and zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof. For example, the second phase material may comprise 40-100 mole percent (more narrowly, at least 70 mole percent or 70-99 mole percent) of such oxide. The oxide may be a mixture of such oxides or a single such oxide. One particular example involves gadolinia as said oxide in a concentration of at least 90%, more particularly, essentially 100% (e.g., with only impurity levels of other components that do not affect performance).

In the exemplary implementation, the second phases may account for 5-15%, more narrowly, 10-13% of the volume of the layer 38 with the matrix 40 accounting for the remainder (ignoring porosity and transitions). In the exemplary combination system, the presence of the base layer 36 provides maximum mechanical strength in the area of the coating where stresses in the coating are maximum.

Coating deposition may be via an otherwise conventional process and apparatus (e.g., EB-PVD or IE-EB-PVD) for depositing coatings such as YSZ and GSZ. An exemplary such system 100 (FIG. 2) comprises a deposition chamber 102 having an interior 104. In this example, the bondcoat has already been deposited (e.g., using another system/chamber). A substrate/part holder 106 may hold the substrate(s) and may be driven by an actuator 108 for rotating the part (e.g., with a period of 2-20 seconds) and/or engaging in more complex manipulations as is discussed below.

A deposition material source comprises two distinct sources (subsources of the matrix 40 and second phases 42). A first source for the matrix 40 comprises an ingot 122 (e.g., of 7YSZ or of slightly altered chemistry so as to yield a 7YSZ layer when subject to attrition of individual components in the vapor cloud/plume). A second source associated with the second phases 42 comprises a second ingot 124. One or more electron guns 126 may be positioned to direct electron beams 128 to exposed surfaces of the ingots to maintain melt pools for generating the vapor cloud 140. The ingots may be contained in respective crucibles 132 and 134.

FIG. 2 schematically shows a stage or mode wherein the electron beam is directed to essentially exclusively vaporize material from the first ingot 122. This may be used for the

deposition of the base layer 36. In this mode and associated stage(s), the vapor cloud 140 consists essentially of material from the first ingot 122. Material from the second ingot 124 may be physically blocked from reaching the substrate by positioning an optional shutter 146 (actuator not shown) between the crucible and the substrate. An exemplary elapsed time during the stage/condition/mode depicted in FIG. 2 would be between 500% and 2000% (5X-20X) of the time period to complete one rotation of the three-dimensional substrate (more broadly, 400-5000%). This allows for the formation of the base layer 36 around the entirety of the coated portion of the part. Where different material or other properties are present in the base layer 36 versus the matrix 40, this step/stage or a similar step/stage may be used to initially deposit an initial portion of the matrix 40.

Next, there may be a small compositional transition in the deposition process. For example, FIG. 3 shows the beam 128 reoriented and directed to the second ingot 124. Initially, the vapor cloud/plume will comprise a residual portion 142 from the first ingot and a portion 144 from the second ingot.

FIG. 4 shows the subsequent stage/mode wherein the beam remains directed to the second ingot 124 and the portion 142 has been expended so that the vapor cloud is essentially derived from the second ingot and not the first ingot so as to deposit the phases 42. Material from the first ingot 122 may be physically blocked from reaching the substrate by positioning an optional shutter 148 (actuator not shown) between the crucible and the substrate. The transition in the vapor deposition process depicted in FIG. 3 would be minimized by rapidly moving the shutter 148 into position immediately as the electron beam is moved from first ingot 122 to second ingot 124.

Because, as described above, the phases 42 are very thin, the elapsed time during the stage/condition/mode depicted in FIG. 4 would be much less than that of the stage/condition/mode depicted in FIG. 2. An exemplary elapsed time during the stage/condition/mode depicted in FIG. 4 would be between 1% and 50% of the time period to complete one rotation of the three-dimensional substrate, or, more narrowly, between 5% and 30% of that time period. Typical time periods to complete one rotation of three-dimensional substrates range from 2 to 20 seconds, or more narrowly 3 to 15 seconds. This allows for the formation of the phases 42 as discrete regions rather than full layers around the entirety of the coated portion of the part.

From the stage/condition/mode depicted in FIG. 4, the system may redirect the beam back to the first ingot (FIG. 5). In the FIG. 5 condition/mode, initially the vapor cloud will comprise residual material 144 from the second ingot and newly-vaporized portion 142 from the first ingot. As the portion 144 is eliminated by blockage by the shutter 146, the condition will revert back to the FIG. 2 stage/condition/mode.

The cycle between depositions from the respective ingots (along with the optional transition stages) may continue until the desired thickness of coating is deposited on the substrate.

An additional coating layer 50 (topcoat, e.g., with a homogeneous chemistry throughout it) may be deposited on top of the matrix 40 with embedded phases 42. The primary role of this topcoat would be to provide resistance to attack by molten silicate deposits that form on the coatings during engine use due to ingestion of dirt. These deposits are

commonly referred to as CMAS (for calcium magnesium aluminosilicate). The additional coating layer broadly comprises a layer of oxyapatite and/or garnet.

Herein, garnet refers broadly to an oxide with the ideal formula of $A_3B_2X_3O_{12}$, where A comprises at least one of the metals selected from the group consisting of Ca, Gd, In, Mg, Na, K, Fe, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y, Ti, Zr, Hf, V, Ta, Cr, W, Mn, Tc, Re, Fe, Os, Co, Ir, Ni, Zn, and Cd; where B comprises at least one of the metals selected from the group consisting of Zr, Hf, Gd, Al, Fe, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, In, Sc, Y, Cr, Sc, V, Nb, Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Ni, and Au; where X comprises at least one of the metals selected from the group consisting of Si, Ti, Al, Fe, Cr, Sc, Y, V, Nb, Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Ni, and Au; and where O is oxygen. Furthermore, limited substitution of S, F, Cl, and OH for oxygen in the above formula is possible in this compound as well, with a concomitant change in the numbers of A, B, and X type elements in the ideal formula, to maintain charge neutrality.

Herein, oxyapatite refers broadly to $A_4B_6X_6O_{26}$ (II) where A comprises at least one of the metals selected from the group consisting of Ca, Mg, Fe, Na, K, Gd, Zr, Hf, Y, Sc, In, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y, Ti, Zr, Hf, V, Ta, Cr, W, Mn, Tc, Re, Fe, Os, Co, Ir, Ni, Zn, and Cd; where B comprises at least one of the metals selected from the group consisting of Gd, Y, Sc, In, Zr, Hf, Cr, Sc, Y, V, Nb, Cr, Mo, W, Mn, Fe, Ru, Co, Rh, Ir, Ni, and Au; where X comprises at least one of the metals selected from the group consisting of Si, Ti, Al, Cr, Sc, Y, V, Nb, Cr, Mo, W, Mn, Fe, Ru, C, Rh, Ir, Ni, and Au; and where O is oxygen. Furthermore, limited substitution of S, F, Cl, and OH for oxygen in the

above formula is possible in this compound as well, with a concomitant change in the numbers of A, B, and X type elements in the ideal formula, to maintain charge neutrality.

As noted above, the coating system and deposition apparatus may be implemented as a modification of an existing coating system and apparatus. The modification may be as simple as merely reprogramming the existing controller of an existing apparatus already used to deposit a two-component TBC (e.g., such as that of the '722 patent). The reprogramming may merely alter the timing of the transitions between deposition stages. Other modifications may involve adding the second source to an existing single-source apparatus.

One or more embodiments have been described. Nevertheless, it will be understood that various modifications may be made. For example, when applied in the reengineering of an existing component and its coating system, details of the existing component and coating system may influence details of any particular implementation. Accordingly, other embodiments are within the scope of the following claims.

CLAIMS

What is claimed is:

1. An article (20) comprising:

a substrate (22); and

a thermal barrier coating system (24) atop the substrate and having a matrix (40) having a first chemistry and a plurality of embedded second phases (42) layered within the matrix having a second chemistry, different from the first chemistry,

wherein:

the matrix comprises a stabilized zirconia;

the second phases comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof;

the second phases have a characteristic thickness (T_6) of less than 2.0 micrometers (μm); and

the spacing between second phases has a characteristic thickness (T_5) of less than 8.0 micrometers (μm).

2. The article of claim 1 wherein:

the matrix comprises a yttria stabilized zirconia; and

the second phases comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

3. The article of claim 1 or claim 2 wherein:

the second phases have characteristic thickness (T_6) of 0.15-1.0μm; and

a ratio of the second phases characteristic thickness (T_6) to the spacing (T_5) between second phases, thickness-wise, is between 1:3 and 1:4.

4. The article of any of claims 1-3 wherein:
the matrix with embedded second phases form a layer having a thickness (T_4) of at least 76 micrometers.

5. The article of any of claims 1-3 wherein:
the matrix with embedded second phases form a layer having a thickness (T_4) of 76-350 micrometers.

6. The article of any of claims 1-5 further comprising:
a bondcoat (28); and
a first TBC layer (36) between the bondcoat and the matrix.

7. The article of any of claims 1-6, wherein:
the first layer has a nominal composition differing from a composition of the matrix by the presence of one or more additives in a total amount of up to 1.0 weight percent.

8. The article of any of claims 1-7 wherein:
the characteristic thickness (T_6) of the second phases is 0.15-1.0 micrometers (μm), and
the characteristic thickness (T_5) of the spacing between second phases is 0.5-3.0 micrometers (μm).

9. The article of any of claims 1-8 further comprising:
an additional coating layer (50) with a homogeneous chemistry atop the matrix with embedded second phases.

10. The article of claim 9 wherein:

the additional coating layer is more resistant to attack by molten silicate deposits than is the matrix.

11. The article of claim 6, further comprising:

an additional coating layer atop the matrix and comprising oxyapatite and/or garnet.

12. The article of claim 1, wherein:

the matrix and second phases are in a layer of the thermal barrier coating system with thickness (T_4) wherein the second phases account for 5-20% of said layer by volume.

13. An article (20) comprising:

a substrate (22); and

a thermal barrier coating system (24) atop the substrate and having a matrix (40) having a first chemistry and a plurality of embedded second phases (42) layered within the matrix having a second chemistry, different from the first chemistry,

wherein:

the embedded second phases within the matrix have a characteristic perimeter extent of 30-85%.

14. The article of claim 13 wherein:

the matrix comprises a yttria stabilized zirconia; and

the second phases comprise at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanides La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

15. The article of claim 13 wherein:

at a given location, a depthwise number of the embedded second regions is 7-84.

16. A process for coating a substrate, the process comprising:

generating a plume (140) of deposition material from a first source (122) and a second source (124);

alternating the composition of the plume by generating vapor from the first and second sources in an alternating manner; and

moving the substrate relative to the first and second sources,

wherein:

the moving of the substrate moves a given region of the substrate through the plume at a cyclic rate having a period greater than a duration of generation of the vapor plume from the second source.

17. The process of claim 16 wherein:

the moving consists of a rotation.

18. The process of claim 16 or 17 wherein:

a duration of generation of the vapor plume from the first source is 400-5000% of said period; and

the duration of generation of the vapor plume from the second source is 30-99% of said period.

19. The process of any of claims 16-18 wherein:

the first source comprises a yttria stabilized zirconia; and

the second source comprises at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanide La through Lu, Y, Sc, In, Ca, and Mg.

20. The process of any of claims 16-18 wherein:

the first source comprises a yttria stabilized zirconia; and

the second source comprises at least 40 mole percent of oxides having the formula Ln_2O_3, where Ln is selected from the lanthanide La through Lu, Y, Sc, In, Ca, and Mg with the balance zirconia (ZrO_2), hafnia (HfO_2), titania (TiO_2), or mixtures thereof.

21. The process of any of claims 16-20 wherein:

the relative speed of the moving and the frequency of alternation of the composition of the vapor plume are effective to deposit a matrix (40) with embedded second phase patches (42) of the coating from the first source and second source, respectively.

22. The process of claim 21 wherein:

each of the second phase patches represents less than 85% of the surface area of the substrate.

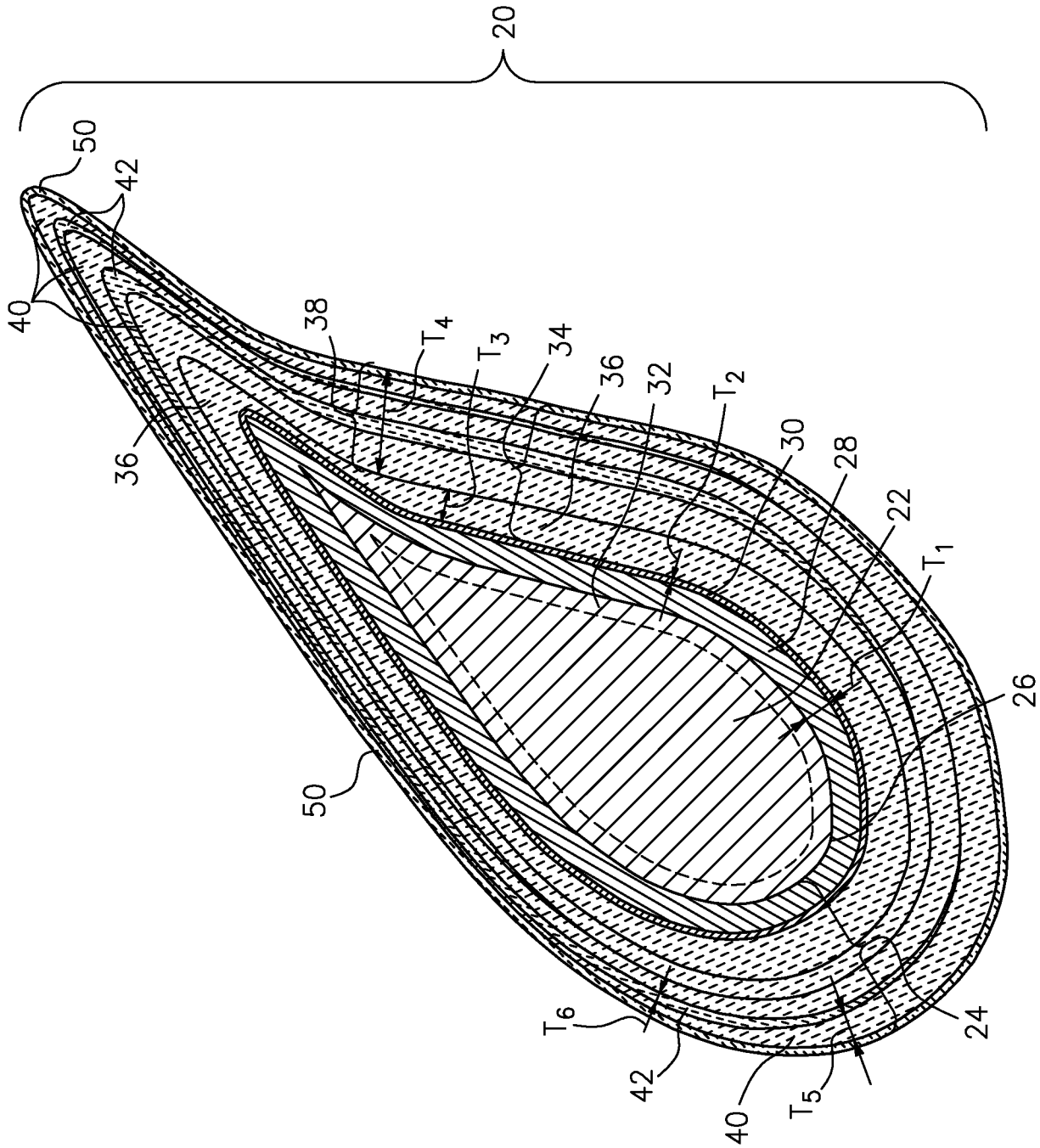

FIG. 1

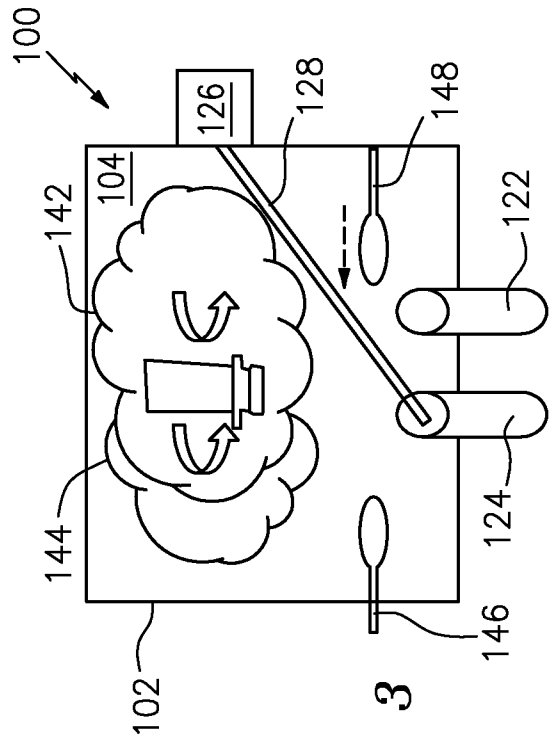

FIG. 3

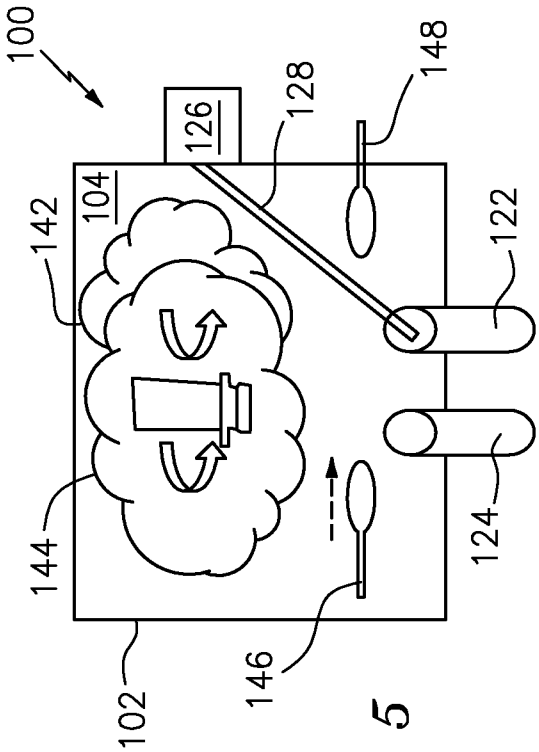

FIG. 5

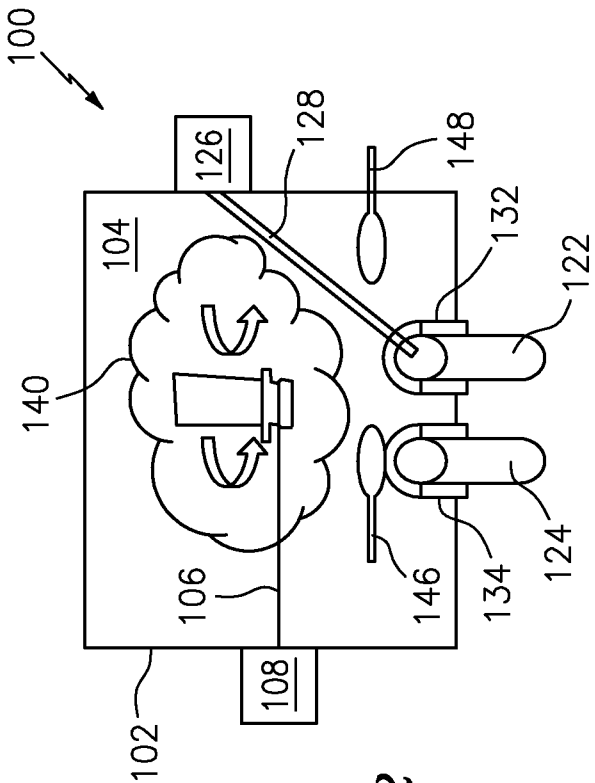

FIG. 2

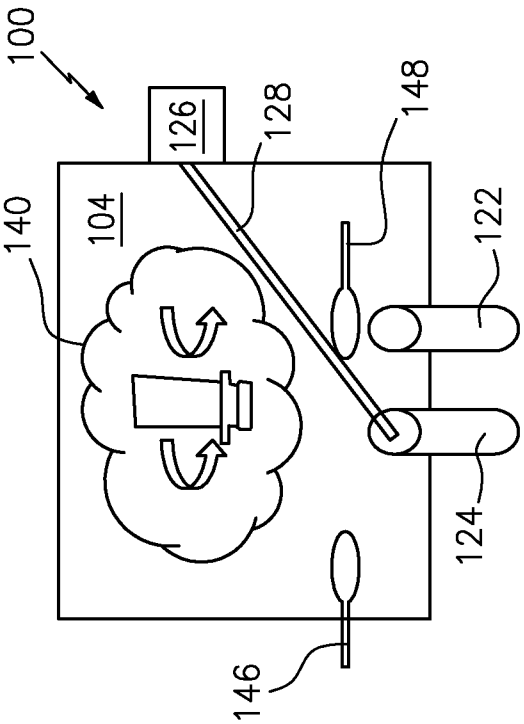

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/028962

A. CLASSIFICATION OF SUBJECT MATTER

B32B 9/00(2006.01)i, B32B 15/04(2006.01)i, B05D 5/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B19/00; B32B9/00; B05D3/06; C23C14/08; C23C14/30; C23C14/48; C23C14/54

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: article, substrate, thermal barrier coating system, matrix

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007-0172703 A1 (FRELING, M. et al.) 26 July 2007. See abstract; claims 1,2,15,29,45; paragraphs [0001],[0002]; and figures 1,2.	1-3,12-18
A	US 2009-0324989 A1 (WITZ, G. E. et al.) 31 December 2009. See abstract; claims 1,2; paragraphs [0048]-[0053]; and figures 1-3.	1-3,12-18
A	US 7838083 B1 (YOUCHISON, D. L. et al.) 23 November 2010. See abstract; claims 1,2; column 3,line 22-column 5,line 10; and figures 1-3.	1-3,12-18
A	US 2008-0057326 A1 (SCHLICHTING, K. W. et al.) 06 March 2008. See abstract; claims 1,2; and paragraphs [0012]-[0016].	1-3,12-18
A	US 2007-0160859 A1 (DAROLIA, R. et al.) 12 July 2007. See abstract, claim 1, paragraph [0028] and figure 1.	1-3,12-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 May 2013 (28.05.2013)	**02 June 2013 (02.06.2013)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
CHANG, Bong Ho
Telephone No. 82-42-481-3353

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/028962

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 10, 11, 22
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The claims listed above are unclear since they are referring to multiple dependent claims which are not drafted in accordance with Rule 6.4(a).

3. ☒ Claims Nos.: 4-9, 19-214-9, 19-21
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/028962

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		EP 1900848 A3	19.08.2009
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US 2007-0160859 A1	12.07.2007	EP 1806435 A2	11.07.2007
		EP 1806435 A3	16.04.2008
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