

LOW THERMAL CONDUCTIVITY, CMAS-RESISTANT THERMAL BARRIER COATINGS

TECHNICAL FIELD

[0001] The present disclosure generally relates to thermal barrier coatings for high-temperature mechanical systems, such as gas turbine engines.

BACKGROUND

[0002] The components of high-temperature mechanical systems, such as, for example, gas-turbine engines, must operate in severe environments. For example, the high-pressure turbine blades and vanes exposed to hot gases in commercial aeronautical engines typically experience metal surface temperatures of about 1000°C, with short-term peaks as high as 1100°C.

[0003] Typical components of high-temperature mechanical systems include a Ni or Co-based superalloy substrate. The substrate can be coated with a thermal barrier coating (TBC) to reduce surface temperatures. The thermal barrier coating may include a thermally insulative ceramic topcoat, and is bonded to the substrate by an underlying metallic bond coat.

[0004] The TBC, usually applied either by air plasma spraying or electron beam physical vapor deposition, is most often a layer of yttria-stabilized zirconia (YSZ) with a thickness of about 100-500 µm. The properties of YSZ include low thermal conductivity, high oxygen permeability, and a relatively high coefficient of thermal expansion. The YSZ TBC is also typically made "strain tolerant" and the thermal conductivity further lowered by depositing a structure that contains numerous pores and/or pathways.

[0005] Economic and environmental concerns, i.e. the desire for improved efficiency and reduced emissions, continue to drive the development of advanced gas turbine engines with higher inlet temperatures. As the turbine inlet temperature continues to increase, there is a demand for a TBC with lower thermal conductivity and higher temperature stability to minimize the increase in, maintain, or even lower the temperatures experienced by the substrate.

SUMMARY

[0006] In general, the present disclosure is directed to a TBC with at least one of lower thermal conductivity or enhanced CMAS-resistance compared to conventional YSZ TBCs. CMAS is a calcia-magnesia-alumina-silicate deposit resulting from the ingestion of siliceous minerals (dust, sand, volcanic ashes, runway debris, and the like) with the intake of air in gas turbine engines.

[0007] In one aspect, the present disclosure is directed to a thermal barrier coating composition including a base oxide comprising zirconia or hafnia; between 2 mol. % and 40 mol. % of a primary dopant including ytterbia; between 0.1 mol. % and 20 mol. % of a first co-dopant including samaria; and between 0.1 mol. % and 20 mol. % of a second co-dopant including at least one of lutetia, scandia, ceria, gadolinia, neodymia, or europia, wherein the thermal barrier coating is essentially free of yttria.

[0008] In another aspect, the present disclosure is directed to a thermal barrier coating composition including a base oxide consisting essentially of zirconia, hafnia, or combinations thereof; between 2 mol. % and 40 mol. % of a primary dopant consisting essentially of ytterbia; between 0.1 mol. % and 20 mol. % of a first co-dopant consisting essentially of samaria; and between 0.1 mol. % and 20 mol. % of a second co-dopant selected from the group consisting of lutetia, scandia, ceria, gadolinia, neodymia, europia, and combinations thereof, wherein the thermal barrier coating is essentially free of yttria.

[0009] In yet another aspect, the present disclosure is directed to an article including a thermal barrier coating applied to at least a portion of a substrate, wherein the thermal barrier coating includes: a base oxide comprising zirconia or hafnia; between 2 mol. % and 40 mol. % of a primary dopant including ytterbia; between 0.1 mol. % and 20 mol. % of a first co-dopant including samaria; and between 0.1 mol. % and 20 mol. % of a second co-dopant including at least one of lutetia, scandia, ceria, gadolinia, neodymia, or europia, wherein the thermal barrier coating is essentially free of yttria.

[0010] The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

[0011] FIG. 1 is a cross-sectional diagram of a substrate coated with a thermal barrier coating including a bond coat and a thermal barrier coating.

[0012] FIG. 2 is a cross-sectional diagram of an alternative embodiment of a substrate coated with only a thermal barrier coating.

[0013] FIG. 3 is a cross-sectional diagram of a substrate coated with a bond coat, environmental barrier coating, and a thermal barrier coating.

[0014] FIG. 4 is a cross-sectional photograph of a CMC substrate coated with a thermal barrier coating bonded to the substrate by an ytterbia-stabilized hafnia on a mullite and silicon bond coat.

[0015] FIG. 5 is a cross-sectional photograph of a CMC substrate coated with a thermal barrier coating bonded to the substrate by an ytterbia-stabilized hafnia on an ytterbium silicate, mullite and silicon bond coat.

[0016] FIG. 6 is a cross-sectional photograph of a CMC substrate coated with a thermal barrier coating including yttrium silicate on a mullite bond coat.

DETAILED DESCRIPTION

[0017] In general, this disclosure is directed to thermal barrier coating (TBC) compositions that possess at least one of reduced thermal conductivity or increased CMAS (calcia-magnesia-alumina-silicate) degradation resistance compared to conventional yttria-stabilized zirconia (YSZ) TBCs, and articles coated with such TBCs. More specifically, the disclosure is directed to a thermal barrier coating including a base oxide, a primary dopant and two co-dopants that possesses at least one of reduced thermal conductivity or increased CMAS degradation resistance compared to conventional YSZ TBCs.

[0018] As turbine inlet temperatures continue to increase, new thermal barrier coatings are required with better high temperature performance. Higher turbine inlet temperatures are detrimental to conventional TBC performance as YSZ may sinter significantly at temperatures above about 1200°C. Sintering reduces the porosity of the YSZ TBC, which may lead to higher thermal conductivity and reduced strain tolerance. Higher thermal conductivity results in the substrate being exposed to higher temperatures, which increases the strain on the substrate and lowers the useful life of the component.

[0019] The reduced strain tolerance of the TBC may also reduce the useful life of the component. For example, the thermal cycles experienced by the component (e.g., ambient temperature when gas turbine is off, high temperature spike when gas turbine is turned on, continuous high temperatures during operation) exert large

stresses on the component due to thermal expansion and contraction. The porosity of the TBC provides strain tolerance, and reduced porosity due to sintering reduces the strain tolerance of the TBC and may compromise the mechanical stability of the TBC and/or TBC-bond coat interface.

[0020] Higher turbine inlet temperatures may also lead to degradation of the TBC through a reaction with CMAS, a calcia-magnesia-alumina-silicate deposit resulting from the ingestion of siliceous minerals (dust, sand, volcanic ashes, runway debris, and the like) with the intake of air in gas turbine engines. Typical CMAS deposits have a melting point of about 1200°C to about 1250°C (about 2200°F to about 2300°F). As advanced engines run at TBC surface temperatures above the CMAS melting point, the molten CMAS can penetrate the microstructural features in the TBC that induce strain tolerance, leading to a loss of strain tolerance and an increase in the thermal conductivity. Another mode of degradation by CMAS is chemical: a reaction between CMAS and yttria in the TBC may occur, preferentially along grain boundaries, leading to the destabilization of YSZ by precipitating monoclinic zirconia (ZrO_2) with a lower yttria content. Both CMAS penetration and YSZ destabilization may result in a shorter life before failure of the component due to higher thermal stresses.

[0021] FIG. 1 shows a cross-sectional view of an exemplary article 10 used in a high-temperature mechanical system. The article 10 includes a coating 14 applied to a substrate 12. The coating includes a bond coat 11 applied to the surface 15 of substrate 12, and a TBC 13 applied to the bond coat 11.

[0022] The substrate 12 may be a component of a high temperature mechanical system, such as, for example, a gas turbine engine or the like. Typical superalloy substrates 12 are alloys based on Ni, Co, Ni/Fe, and the like. The superalloy substrate 12 may include other additive elements to alter its mechanical properties, such as toughness, hardness, temperature stability, corrosion resistance, oxidation resistance, and the like, as is well known in the art. Any useful superalloy substrate 12 may be utilized, including, for example, those available from Martin-Marietta Corp., Bethesda, MD, under the trade designation MAR-M247; those available from Cannon-Muskegon Corp., Muskegon, MI, under the trade designation CMSX-4, CMXS-10; and the like.

[0023] The substrate 12 may also include a ceramic matrix composite (CMC). The CMC may include any useful ceramic matrix material, including, for example, silicon carbide, silicon nitride, alumina, silica, and the like. The CMC may further include any desired filler material, and the filler material may include a continuous reinforcement or a discontinuous reinforcement. For example, the filler material may comprise discontinuous whiskers, platelets, or particulates. As another example, the filler material may include a continuous monofilament or multifilament weave.

[0024] The filler composition, shape, size, and the like may be selected to provide the desired properties to the CMC. For example, in some embodiments, the filler material may be chosen to increase the toughness of a brittle ceramic matrix. In other embodiments, the filler may be chosen to provide a desired property to the CMC, such as thermal conductivity, electrical conductivity, thermal expansion, hardness, or the like.

[0025] The filler composition may be the same as the ceramic matrix material. For example, a silicon carbide matrix may surround silicon carbide whiskers. In other embodiments, the filler material may comprise a different composition than the ceramic matrix, such as aluminum silicate fibers in an alumina matrix, or the like. One preferred CMC includes silicon carbide continuous fibers embedded in a silicon carbide matrix.

[0026] The article 10 may include a bond coat 11. The bond coat 11 may improve adhesion between the TBC 13 and the substrate 12. The bond coat 11 may include any useful alloy, such as a conventional MCrAlY alloy (where M is Ni, Co, or NiCo), a β -NiAl nickel aluminide alloy (either unmodified or modified by Pt, Cr, Hf, Zr, Y, Si, and combinations thereof), a γ -Ni + γ' -Ni₃Al nickel aluminide alloy (either unmodified or modified by Pt, Cr, Hf, Zr, Y, Si, and combinations thereof), or the like.

[0027] The bond coat 11 may also include ceramics or other materials that are compatible with a CMC substrate 12. For example, the bond coat 11 may include mullite (aluminum silicate, Al₆Si₂O₁₃), silica, silicides, silicon, or the like. The bond coat 11 may further include other ceramics, such as rare earth silicates including lutetium silicates (Lu; Lutetium), ytterbium silicates (Yb; Ytterbium),

erbium silicates (Er: Erbium), dysprosium silicates (Dy: Dysprosium), gadolinium silicates (Gd: Gadolinium), europium silicates (Eu: Europium), samarium silicate (Sm: Samarium), neodymium silicates (Nd: Neodymium), yttrium silicates (Y: Yttrium), scandium silicates (Sc: Scandium), or the like. Some preferred bond coat 11 compositions for overlaying a CMC substrate 12 include silicon, mullite and ytterbium silicate.

[0028] The bond coat 11 may be selected based on a number of considerations, including the chemical composition and phase constitution of the TBC 13 and the substrate 12. For example, when the substrate 12 includes a superalloy with γ -Ni + γ' -Ni₃Al phase constitution, the bond coat 11 preferably includes a γ -Ni + γ' -Ni₃Al phase constitution to better match the coefficient of thermal expansion of the superalloy substrate 12, and therefore increase the mechanical stability (adhesion) of the bond coat 11 to the substrate 12. Alternatively, when the substrate 12 comprises a CMC, the bond coat 11 is preferably silicon and/or a ceramic, such as, for example, mullite or rare earth silicates.

[0029] In some embodiments, the bond coat 11 may include multiple layers. For example, in some embodiments where the substrate 12 is a CMC including silicon carbide, a first bond coat of silicon is deposited on the CMC substrate 12, followed by the deposition of a second layer including mullite (aluminum silicate, Al₆Si₂O₁₃) or a rare earth silicate. The multilayer bond coat is desirable because the silicon bond coat provides the bonding while the ceramic bond coat provides a gradual transition of thermal expansion and prevents water vapor from reaching the silicon bond coat.

[0030] In other embodiments, such as the article 20 illustrated in FIG. 2, the article 20 may not include a bond coat 11. For example, in some embodiments, the TBC 23 may be applied directly to the substrate 22. A bond coat 11 may not be required or desired when the TBC 23 and the substrate 22 are chemically and/or mechanically compatible. For example, in embodiments where the TBC 23 and substrate 22 adhere sufficiently strongly to each other, a bond coat 11 may not be necessary. Additionally, in embodiments where the coefficients of thermal expansion of the substrate 22 and TBC 23 are sufficiently similar, a bond coat 11 may not be necessary.

[0031] As shown in FIG. 3, an article 30 may also include an environmental barrier coating (EBC) 36 applied to the bond coat 31. In this embodiment, the TBC 33 is applied to the EBC 36. Environmental barrier coatings may provide water vapor stability, chemical stability, and environmental durability to substrates, such as, for example, CMC. Environmental barrier coatings may include, for example, barium strontium alumina silicate ($\text{BaO-SrO-Al}_2\text{O}_3\text{-2SiO}_2$; BSAS), rare earth silicates, combinations thereof, and the like.

[0032] In alternative embodiments (not pictured) the EBC 36 may be directly applied to a CMC substrate 32. In these embodiments, the EBC 36 may also perform the function of the bond coat 31 and increase the adhesion between the TBC 33 and the CMC substrate 32. A preferred combination EBC 36 and bond coat 31 layer includes mullite and rare earth silicates.

[0033] As was described briefly above, one purpose of the TBC 13, 23, 33 (collectively "TBC 13") is to provide thermal insulation for the substrate from high temperatures of the turbine gas. Because of this, it is desirable that the TBC 13 has a low thermal conductivity (both an intrinsic thermal conductivity of the material(s) that forms TBC 13 and an effective thermal conductivity of the TBC 13 as constructed). Heat is transferred through the TBC 13 through conduction and radiation. The inclusion of rare earth elements such as ytterbia, samaria, lutetia, scandia, ceria, gadolinia, neodymia, europia, and the like as dopants may help decrease the thermal conductivity (by conduction) of the TBC 13. While not wishing to be bound by any specific theory, the inclusion of at least one of these dopant ions in the TBC 13 may reduce thermal conductivity through one or more mechanisms, as follows.

[0034] A first proposed mechanism of reducing thermal conductivity includes introducing lattice imperfections into the crystal structure of the TBC 13. Lattice imperfections include defects in the crystalline lattice of the TBC 13. The defects may be caused by the incorporation of dopants with differing ionic radii or different crystalline lattice types. Lattice imperfections may be broadly divided into two categories, point defects and larger defects, for the purposes of this discussion. The point defects, such as substitutional defects, interstitial defects, void defects, and the like, may scatter high frequency phonons (lattice waves),

while larger defects, such as grain boundaries of crystals that are smaller than about 100 nm, may scatter lower frequency phonons. In either case, phonon scattering decreases the thermal conductivity of the TBC 13 by reducing the mean free path of a phonon (i.e., the average distance the phonon travels between scattering sites).

[0035] Heavier rare earth oxide dopants are expected to lower the thermal conductivity more than lighter rare earth oxide dopants. For example, rare earth oxides including ytterbia, lutetia, gadolinia, samaria, neodymia, europia, and the like are expected to more effectively lower the thermal conductivity of a TBC 13 than yttria.

[0036] Inclusion of certain rare earth elements in the TBC 13 may also decrease the extent to which the TBC 13 sinters at a given temperature. For example, incorporating rare earth elements with a larger ionic radius than yttrium can decrease the amount of sintering at a given temperature. While not wishing to be bound by any theory, a larger ionic radius can lead to a lower diffusion coefficient at a given temperature. As sintering is primarily a diffusion-related process, a lower diffusion coefficient lowers the amount of sintering at a given temperature.

[0037] Minimizing or eliminating sintering may significantly improve the stability of the thermal conductivity of the TBC 13 over the service life of the TBC 13. Thermal conductivity of the TBC 13 is typically lowered by depositing the TBC 13 as a porous structure. The porosity of the TBC 13 reduces the thermal conductivity by reducing the area through which heat is conducted and by providing a large refractive index difference between the pores and the material from which the TBC 13 is made, which can reduce heat transfer by radiation. Sintering reduces the porosity of the structure, and thus increases the thermal conductivity (via both radiation and conduction) of the TBC 13. Thus, preserving the porosity (i.e., reducing sintering) of the TBC 13 over repeated thermal cycles may help maintain the thermal conductivity of the TBC 13 at or near the level of the originally-applied TBC 13.

[0038] The TBC 13 compositions of the present disclosure may also improve another significant shortcoming of conventional YSZ TBCs. Specifically, CMAS is highly reactive with yttria in the TBC 13, preferentially along grain boundaries,

leading to the destabilization of YSZ by precipitating monoclinic zirconia (ZrO_2) with a lower yttria content, which may result in a shorter life before failure of the component due to higher thermal stresses. Thus, it may be particularly desirable to form a TBC 13 that is substantially free of yttria. Substantially free of yttria means the exclusion of any amount of yttria greater than that present in the commercially-available forms of the other rare earth oxides or base oxides used in the TBC 13.

[0039] Other rare earth elements, including ytterbia, lutetia, and scandia, for example, are more chemically stable in the presence of CMAS. Thus, these elements, either alone or in combination, may desirably replace yttria as the primary dopant in a TBC 13, which may reduce or slow the destabilization of TBC13 in the presence of CMAS.

[0040] The TBC 13 of the current disclosure generally includes a base oxide, a primary dopant, a first co-dopant, and a second co-dopant. Including multiple dopants, preferably of different ionic radii, may decrease the thermal conductivity of the TBC 13 more than a single dopant when present at the same total concentration. For example, the differing ionic radii may increase the elastic strain field caused by the lattice imperfections.

[0041] The base oxide of the TBC 13 may include or may consist essentially of zirconia, hafnia, and combinations thereof. In the current disclosure, to “consist essentially of” means to consist of the listed element(s) or compound(s), while allowing the inclusion of impurities present in small amounts such that the impurities do not substantially affect the properties of the listed element or compound. For example, the purification of many rare earth elements is difficult, and thus the nominal rare earth element may include small amounts of other rare earth elements. This mixture is intended to be covered by the language “consist essentially of.” Many conventional TBCs 13 are based on zirconia, so the processing and production of TBCs 13 including zirconia are well-understood, but hafnia-based TBCs are expected to have a lower thermal conductivity due to a higher mean atomic weight, which is one factor in thermal conductivity.

[0042] The composition of the TBC 13 may be selected to provide a metastable tetragonal (t'), cubic (c), or a mixture of tetragonal and cubic ($t' + c$) phase constitution. A metastable tetragonal phase constitution is generally preferred.

[0043] The primary dopant is generally selected to provide increased resistance to CMAS attack. The primary dopant may include ytterbia, or may consist essentially of ytterbia. The TBC 13 composition may include the primary dopant in concentrations from about 2 mol. % to about 40 mol. %. Preferred primary dopant concentrations range from about 2 mol. % to about 20 mol. %, and about 2 mol. % to about 10 mol. % primary dopant is most preferred. The primary dopant is preferably present in a greater amount than either the first or second co-dopants, and may be present in an amount less than, equal to, or greater than the total amount of the first and second co-dopants.

[0044] The first and second co-dopants are generally selected to provide decreased thermal conductivity compared to YSZ and increased resistance to sintering. The first co-dopant may comprise samaria, or may consist essentially of samaria. The TBC 13 composition may include the first co-dopant in concentrations from about 0.1 mol. % to about 20 mol. %, preferably about 0.5 mol. % to about 10 mol. %, most preferably about 0.5 mol. % to about 5 mol. %.

[0045] The second co-dopant may include lutetia (Lu_2O_3), scandia (Sc_2O_3), ceria (CeO_2), gadolinia (Gd_2O_3), neodymia (Nd_2O_3), europia (Eu_2O_3), and combinations thereof. In other embodiments, the second co-dopant may be selected from the group consisting of lutetia (Lu_2O_3), scandia (Sc_2O_3), ceria (CeO_2), gadolinia (Gd_2O_3), neodymia (Nd_2O_3), europia (Eu_2O_3), and combinations thereof. The second co-dopant may be present in the TBC 13 in an amount ranging from about 0.1 mol. % to about 20 mol. %, preferably about 0.5 mol. % to about 10 mol. %, most preferably about 0.5 mol. % to about 5 mol. %.

[0046] The composition of the TBC 13 may be chosen to provide a desired phase constitution. Accessible phase constitutions include metastable tetragonal t' , cubic (c), and $\text{RE}_2\text{O}_3\text{-ZrO}_2$ (and/or HfO_2) compounds, such as $\text{RE}_2\text{Zr}_2\text{O}_7$ and $\text{RE}_2\text{Hf}_2\text{O}_7$ (where RE is a rare earth element). To achieve a $\text{RE}_2\text{O}_3\text{-ZrO}_2$ (and/or HfO_2) compound phase constitution, the TBC 13 includes about 20 mol. % to about 40 mol. % primary dopant, about 10 mol. % to about 20 mol. % first co-dopant, about 10 mol. % to about 20 mol. % second co-dopant, and the balance base oxide and any impurities present. To achieve a cubic phase constitution, the TBC 13 includes about 5 mol. % to about 20 mol. % primary dopant, about 2 mol. % to about 10

mol. % first co-dopant, about 2 mol. % to about 10 mol. % second co-dopant, and the balance base oxide and any impurities present. In some embodiments, the TBC 13 composition is preferably selected to provide a metastable tetragonal t' phase constitution.

[0047] The TBC 13 may be applied by any useful coating method, however, preferred methods include plasma spraying and electron beam physical vapor deposition (EB-PVD). Plasma spraying is generally preferred when a lower thermal conductivity is desired due to the greater prevalence of disk-shaped pores oriented with a major axis perpendicular to the temperature gradient, which decreases the thermal conductivity of the TBC 13. EB-PVD is preferred when higher strain tolerance is desired due to the columnar structure in the TBC 13 that impart greater strain tolerance than plasma-sprayed microstructure.

[0048] TBCs 13 of the present disclosure may provide at least one of a decreased thermal conductivity and an increased resistance to CMAS attack. The TBC 13 of the current disclosure may also enable higher gas turbine operating temperatures, up to about 1650°C.

EXAMPLES

Example 1: Ytterbia-Stabilized Hafnia (YbSH) TBC on CMC

[0049] FIG. 4 shows a cross-sectional view of an article 40 including an ytterbia-stabilized hafnia (YbSH) TBC 42 on a silicon 49 / mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) 48 bond coat 44 applied on CMC substrate 46. The article 40 was exposed to 300 one hour thermal cycles at 1300 °C and 90% water vapor prior to the photograph. Despite the relatively high coefficient of thermal expansion (CTE) of YbSH (about $10 \times 10^{-6}/^\circ\text{C}$ for YbSH versus about $4 \times 10^{-6}/^\circ\text{C}$ to about $5 \times 10^{-6}/^\circ\text{C}$ for CMC), the multilayer coating having the YbSH TBC 42 maintained excellent adherence, protecting the CMC substrate 46 from water vapor attack. The propensity of through-thickness cracking is believed to have relieved the CTE mismatch stress. Adding the YbSH TBC 42 reduced the thermal conductivity by about 34% from the baseline environmental barrier coating, from about 2 W/m-K to about 1.3 - 1.4 W/m-K.

Example 2: YbSH/Ytterbium Silicate TBC on CMC

[0050] FIG. 5 shows a cross-sectional view of an article 50 including an ytterbia-stabilized hafnia (YbSH) TBC 52 on a silicon 59 / mullite 58 / ytterbium silicate 57 bond coat 54. The bond coat is applied on a CMC substrate 56. The article 50 was exposed to 100 one hour thermal cycles at 1300 °C and 90% water vapor prior to the photograph. The TBC 52 again maintained excellent adherence to the substrate 56.

Example 3: Yttrium Silicate on Mullite Bond-coated CMC

[0051] FIG. 6 shows a cross-sectional view of an article 60 including an yttrium silicate TBC 62 on a mullite bond coat. The mullite bond coat was applied to a silicon carbide substrate 66. The article 60 was exposed to 46 one hour thermal cycles at 1400 °C and 90% water vapor prior to the photograph. The mullite bond coat and yttrium silicate reacted to form the glassy bubbles 67, severely damaging the TBC 62. A similar glass formation reaction due to yttria-mullite reaction was observed when the yttrium silicate was replaced with an yttria-stabilized zirconia TBC. Mullite-ytterbium silicate does not show glass formation in the same condition, suggesting a superior chemical stability of ytterbia compared to yttria in the presence of CMAS.

[0052] Various embodiments of the invention have been described. These and other embodiments are within the scope of the following claims.

CLAIMS:

1. A thermal barrier coating composition comprising:
a base oxide comprising zirconia or hafnia;
5 between 2 mol. % and 40 mol. % of a primary dopant comprising ytterbia;
between 0.1 mol. % and 20 mol. % of a first co-dopant comprising samaria; and
between 0.1 mol. % and 20 mol. % of a second co-dopant comprising at least
one of lutetia, scandia, ceria, gadolinia, neodymia, or europia, wherein the thermal
barrier coating is essentially free of yttria.
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2. The thermal barrier coating composition of claim 1, wherein the primary dopant
is present in a larger amount than either of the first co-dopant and the second co-dopant.
3. The thermal barrier coating composition of claim 1, wherein the thermal barrier
15 coating comprises 2 mol. % to 20 mol. % of the primary dopant, 0.5 mol. % to 10 mol.
% of the first co-dopant, 0.5 mol. % to 10 mol. % of the second co-dopant, and the
balance base oxide and impurities.
4. The thermal barrier coating composition of claim 1, wherein the thermal barrier
20 coating comprises 2 mol. % to 10 mol. % of the primary dopant, 0.5 mol. % to 5 mol. %
of the first co-dopant, 0.5 mol. % to 5 mol. % of the second co-dopant, and the balance
base oxide and impurities.
5. The thermal barrier coating composition of claim 1, wherein the thermal barrier
25 coating comprises at least one of a cubic phase constitution or a tetragonal t' phase
constitution.

6. The thermal barrier coating composition of claim 1, wherein the thermal barrier coating comprises $\text{RE}_2\text{O}_3\text{-ZrO}_2$ compounds, $\text{RE}_2\text{O}_3\text{-HfO}_2$ compounds and combinations thereof, and wherein RE is a rare earth element.

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7. The thermal barrier coating composition of claim 1, wherein the thermal barrier coating comprises a mixture of a cubic phase constitution and a $\text{RE}_2\text{O}_3\text{-ZrO}_2$ compound, $\text{RE}_2\text{O}_3\text{-HfO}_2$ compounds and combinations thereof, and wherein RE is a rare earth element.

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8. The thermal barrier coating composition of any of claims 1 to 7, wherein:
the base oxide consists essentially of zirconia, hafnia, or combinations thereof;
the primary dopant consists essentially of ytterbia;
the first co-dopant consists essentially of samaria; and
15 the second co-dopant selected from the group consisting of lutetia, scandia, ceria, gadolinia, neodymia, europia, and combinations thereof.

9. An article comprising:
a substrate; and

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the thermal barrier coating of any of claims 1 to 8, wherein the thermal barrier coating is applied to at least a portion of a substrate.

10. The article of claim 9, further comprising a bond coat applied to at least a portion of the substrate, wherein the thermal barrier coating is applied to the bond coat.

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11. The article of claim 9, further comprising an environmental barrier coating

applied to at least a portion of the substrate, wherein the thermal barrier coating is applied to the environmental barrier coating.

12. The article of claim 9, further comprising a bond coat applied to at least a
5 portion of the substrate and an environmental barrier coating applied to the bond coat,
wherein the thermal barrier coating is applied to the environmental barrier coating.