



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
13.04.2011 Bulletin 2011/15

(51) Int Cl.:
C23C 18/12 (2006.01)

(21) Application number: **10186959.2**

(22) Date of filing: **08.10.2010**

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

- **Ruud, James Anthony**
Niskayuna, NY 12309 (US)
- **Szala, Lawrence Edward**
Niskayuna, NY 12309 (US)
- **Manoharan, Mohan**
560066, Bangalore (IN)
- **Willson, Patrick Daniel**
Niskayuna, NY 12309 (US)

(30) Priority: **12.10.2009 US 577416**

(71) Applicant: **General Electric Company**
Schenectady, NY 12345 (US)

(74) Representative: **Szary, Anne Catherine et al**
GE International Inc.
Global Patent Operation - Europe
15 John Adam Street
London
WC2N 6LU (GB)

(72) Inventors:
• **McEvoy, Kevin Paul**
Niskayuna, NY 12309 (US)

(54) **Process of forming a coating system, coating system formed thereby, and components coated therewith**

(57) A process by which a ceramic coating (14) is entirely formed from a colloidal-based process to have a thickness that would ordinarily be prone to cracks and spallation involves forming a precursor primer layer on a surface region (12,16,18), and then forming at least a precursor coating layer on the precursor primer layer that is thicker than the precursor primer layer. The precursor primer layer contains particles and a precursor of a first

ceramic material. The precursor coating layer contains particles and a precursor of a second ceramic material having the same predominant constituent as the first ceramic material. The precursor primer layer and precursor coating layer are then heated to form a ceramic film (20) and a ceramic coating layer (14), respectively, which consist essentially of the particles and matrices of, respectively, the first and second ceramic materials.

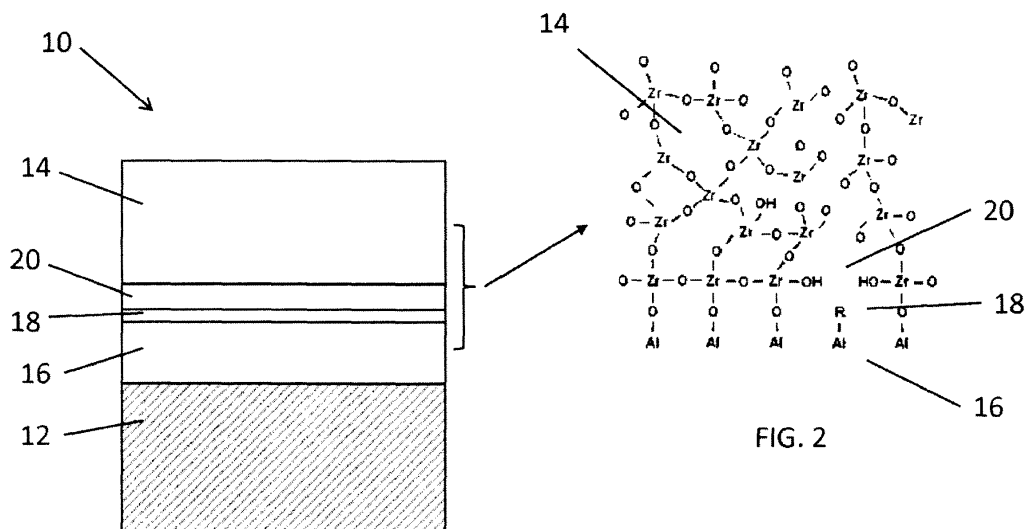


FIG. 1

FIG. 2

Description

BACKGROUND OF THE INVENTION

[0001] The present invention generally relates to coating systems and methods for their deposition. More particularly, this invention relates to a process for forming a ceramic coating using a colloidal-based process, such as a sol (colloidal suspension) or sol-gel, and particularly a process in which the entire ceramic coating is formed from a colloidal-based process to have a thickness that would ordinarily crack and spall when deposited on a metallic substrate and subjected to thermal cycling. Resistance to cracking and spallation are promoted with a ceramic film of limited thickness and formed from a sol or slurry containing particles having narrowly tailored size, reactivity and composition.

[0002] The maximum turbine inlet temperature of a gas turbine is limited by the ability of the hot gas path components, especially turbine components such as vanes and blades, to withstand the heat, oxidation and corrosion effects of the hot gas stream and maintain sufficient mechanical strength. Consequently, there exists a continuing need to find advanced material systems for use in components that will function satisfactorily in high performance gas turbines that operate at higher temperatures and stresses. A common approach is to protect surfaces of components with environmentally and thermally protective coating systems. Such coating systems typically include a metallic bond coat that environmentally protects the component surface and adheres a thermal barrier coating (TBC) that provides an insulating effect but offers little resistance to oxidation, erosion, and corrosion. TBC's are typically formed of a ceramic material, a widely-used example of which is yttria-stabilized zirconia (YSZ). The ability of a metallic bond coat to adhere a ceramic TBC and protect the underlying substrate is typically promoted through the formation of an adherent oxide scale, such as a thin layer of aluminum oxide (alumina), on its surface, which chemically bonds the ceramic TBC to the bond coat. For this purpose, various bond coats have been proposed, notable examples of which include diffusion coatings that contain aluminum intermetallics (predominantly beta-phase nickel aluminide (β -NiAl) and platinum aluminides (PtAl)), and overlay coatings such as MCrAlX (where M is iron, cobalt and/or nickel, and X is yttrium, rare earth metals, and/or reactive metals).

[0003] The service lives of coating systems of the type described above are typically limited at high temperatures due to excessive growth of the oxide scale on the bond coat and flaws which develop within the interfacial zone between the bond coat and ceramic TBC. Thermally-induced deterioration of the interfacial zone coupled with stresses induced by thermal transients, thermal expansion mismatch between the ceramic TBC and the metallic bond coat and substrate, and oxide growth eventually lead to spallation of the TBC. Considerable advances

have been made in the spallation resistance of TBCs through processing and compositional modifications to bond coats and TBCs, which are typically deposited by techniques such as thermal spraying and physical vapor deposition (PVD), particularly electron beam physical vapor deposition (EBPVD). However, these techniques have disadvantages and limitations, such as relatively high costs and being limited to line-of-sight deposition, the latter of which complicates the ability to protect components such as nozzle doublets that have complex geometries.

[0004] One approach being explored to overcome these disadvantages and limitations is the use of sol-based and colloidal-based processes, including sol-gels, to deposit TBCs. As well known in the art, colloidal-based processes entail depositing multiple layers of a liquid precursor, such as a metal alkoxide, metal chloride, or organometallic, of the desired ceramic for the TBC. The precursor may also contain particles of the desired ceramic (often referred to as a colloid). After drying, the deposited layers are heated to convert the precursor to the desired ceramic. Deposition of the precursor layers can be by immersion, spraying, brushing, etc., which allow the coating of surfaces that would be otherwise difficult to coat by a line-of-sight process. However, TBCs and other ceramic coatings formed from colloidal-based processes typically exhibit low tensile adhesion and cracking. For example, the microphotographs of FIGS. 3 and 4 evidence poor adhesion and through-cracks in a YSZ TBC having a thickness of about 100 micrometers. The coating was formed on a PtAl diffusion bond coat by a sol-gel process using zirconium chloride hexahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and yttrium methoxide ($\text{C}_9\text{H}_{21}\text{O}_6\text{Y}$) as precursors for zirconia (ZrO_2) and yttria (Y_2O_3), respectively, in which particles (d50 of about 130 nm) of YSZ (8 molar percent yttria) were dispersed. These coatings also tend to prematurely spall when subjected to thermal cycling, as evidenced by the microphotograph of FIG. 5, which shows a YSZ TBC formed by the same process as that used to form the coating of FIGS. 3 and 4. The coating had been subject to thermal cycling employing one-hour cycles between room temperature and about 2000°F (about 1090°C), and had sustained about twenty percent spallation at the completion of about sixty cycles.

[0005] There are ongoing efforts to enhance the bonding of colloidal-based coatings. Typical examples include treatments to roughen, oxidize, or adjust the pH of the substrate surface to increase bond strength. These methods have been met with limited success, and therefore additional and alternative steps have been tried as well, such as the use of chemically compatible bond coats and the application of a thin film of alumina to the bond coat prior to applying the TBC coating, the latter of which is intended to enhance the growth of oxide into the TBC coating. However, these methods have also achieved limited success, with the result that ceramic coatings deposited by sol-gel and other colloidal-based processes are typically limited to thicknesses of not greater than

about 50 micrometers, and often less than 25 micrometers.

BRIEF DESCRIPTION OF THE INVENTION

[0006] The present invention provides coating systems and colloidal-based coating processes, by which a ceramic coating can be entirely formed from a colloidal-based process to have a thickness that would ordinarily crack and spall when deposited on a metallic substrate and subjected to thermal cycling. Resistance to cracking and spallation are promoted through the inclusion of a ceramic film that is formed to have a limited thickness and contain ceramic particles having narrowly tailored size, reactivity and composition.

[0007] According to a first aspect of the invention, the process includes forming a precursor primer layer on and contacting a surface region of a component, and then forming at least one precursor coating layer on and contacting the precursor primer layer. The precursor primer layer has a thickness of up to about 30 micrometers and comprises a precursor of a first ceramic material having a predominant constituent and a dispersion of particles of the first ceramic material. The particles of the precursor primer layer have a median particle size (d₅₀) of about 20 to about 100 nanometers. The precursor coating layer has a thickness of greater than the precursor primer layer and comprises a precursor of a second ceramic material having the same predominant constituent as the first ceramic material and a dispersion of particles of the second ceramic material. The precursor primer and coating layers are then heated to form a ceramic film from the precursor primer layer and a ceramic coating layer from the precursor coating layer. The ceramic film has a thickness of up to 30 micrometers and consists essentially of the particles of the first ceramic material in a matrix of the first ceramic material. The ceramic coating layer has a thickness of greater than the ceramic film and consists essentially of the particles of the second ceramic material in a matrix of the second ceramic material.

[0008] Another aspect of the invention is a coating system formed by the process described above, as well as components protected by such a coating system. The ceramic coating layer of the coating system may be, as nonlimiting examples, a TBC, a corrosion or erosion mitigation coating, a hermetic seal, etc., and applied to gas turbine components as well as a wide variety of other components that benefit from a ceramic coating

[0009] A notable aspect of the process and the resulting coating system is that the particle size and thickness of the precursor primer layer and the thickness of the resulting ceramic film are limited to achieve sufficient adhesion of the ceramic coating layer that enables the ceramic coating layer to resist spallation and survive thermal cycling when applied to thicknesses of up to at least 200 micrometers. The effectiveness of the ceramic film has been shown by producing and testing coating systems with and without the ceramic film of this invention,

with those including the ceramic film being able to exhibit thermal cycle lives of at least four times greater than those without. The ability of the ceramic film to provide a robust platform and bond for thick ceramic coatings applied by colloid-based processes enables a significant cost advantage relative to PVD and other typical processes that are commonly employed to deposit TBCs and similar thick ceramic coatings, but are limited by line-of-sight and other geometric constraints.

[0010] Other aspects and advantages of this invention will be better appreciated from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 schematically represents a cross-sectional view of a substrate having a coating system according to an embodiment of the present invention, in which a ceramic film adheres a ceramic coating to a metallic bond coat on the substrate.

[0012] FIG. 2 is a representation of the chemical composition of the ceramic film and the ceramic coating of FIG. 1.

[0013] FIG. 3 is a microphotograph of a ceramic coating formed from a sol-gel in accordance with prior art practices.

[0014] FIG. 4 is a magnified microphotograph of the ceramic coating of FIG. 3, evidencing poor adhesion and through-cracks in the coating as deposited.

[0015] FIG. 5 is a microphotograph of the ceramic coating of FIG. 3 following thermal cycling, evidencing further cracking and spallation of the coating.

[0016] FIG. 6 is a microphotograph of a ceramic coating formed from a sol-gel and deposited on a ceramic film in accordance with an embodiment of the present invention.

[0017] FIG. 7 is a magnified microphotograph of the ceramic coating of FIG. 6, evidencing that the ceramic coating is essentially crack-free and well-adhered to the ceramic film as deposited.

[0018] FIG. 8 is a microphotograph of the ceramic coating of FIG. 6 following thermal cycling, evidencing that the ceramic coating remained essentially crack-free and well-adhered to the ceramic film.

[0019] FIGS. 9, 10 and 11 summarize test specimens and results obtained during investigations leading to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] FIG. 1 schematically represents a metallic substrate region 12 of a component 10, which may be a gas turbine engine component, particular examples of which include hot gas path components such as turbine blade and turbine vanes, though other applications are also foreseeable and within the scope of the invention. The substrate region 12 is shown protected by a coating system that includes an outer ceramic coating 14 adhered

to the substrate region 12 by a metallic bond coat 16. The substrate region 12 is preferably a metallic material, for example, a nickel-base or cobalt-base superalloy, though various other materials can also be protected in accordance with the invention. FIG. 1 depicts the bond coat 16 as having a continuous and adherent oxide scale 18 on its surface to promote the adhesion of the ceramic coating 14 to the bond coat 16 and the underlying substrate region 12. The oxide scale 18 can be formed by subjecting the bond coat 16 to an oxidizing environment, such that the scale 18 may be termed a thermally-grown oxide (TGO). The thickness of the oxide scale 18 will vary depending on the composition and processing of the bond coat 16, though thicknesses of about 100 to about 500 nanometers are typical and acceptable. The bond coat 16 is preferably present in the coating system to provide environmental protection to the underlying substrate region 12 of the component 10, though in some cases the bond coat 16 could be omitted if the composition of the substrate region 12 is sufficiently resistant to oxidation, corrosion, or other sources of environmental attack, and/or is capable of forming a continuous and adherent oxide scale on its surface.

[0021] The bond coat 16 is preferably an aluminum-containing composition capable of forming alumina as the oxide scale 18 on its surface when subjected to an oxidizing environment, though the use of other bond coat compositions is also foreseeable. Preferred compositions for the bond coat 16 include aluminide coatings such as a platinum-modified aluminide (PtAl) diffusion coating or a beta-phase (NiAl) nickel aluminide overlay coating, though the use of other bond coat compositions is foreseeable, for example, an MCrAlX overlay coating alloy (where M is iron, cobalt and/or nickel, and X is yttrium, rare earth metals, and/or reactive metals). As known in the art, if the bond coat 16 is a diffusion aluminide coating, a suitable process for forming bond coat 16 is to deposit and diffuse aluminum into the surface of the substrate region 12 to form aluminide intermetallics on and beneath the surface of the substrate region 12. If the bond coat 16 is an overlay coating, the desired composition for the bond coat 16 can be directly deposited on the surface of the substrate region 12 by plasma spraying or another physical vapor deposition (PVD) process, with minimal interdiffusion with the substrate region 12. It is contemplated that other processes could be used to apply the bond coat 16 to the substrate region 12. The thickness of the bond coat 16 will depend on its composition and type. For PtAl and NiAl bond coats, a typical thickness is up to about 20 micrometers, for example, about 4 to about 12 micrometers. Other aspects of bond coats, including their compositions and deposition processes, are well known in the prior art and therefore will not be described in any further detail here.

[0022] The ceramic coating 14 may be employed as a thermal barrier coating (TBC), a corrosion or erosion mitigation coating, a hermetic seal, or any other application in which an adherent ceramic coating could be utilized.

Typical materials for TBCs include ceramics, and particularly zirconia (ZrO_2) at least partially stabilized with yttria (Y_2O_3) (for example, about 4 to about 20 weight percent yttria), though the use of other or additional stabilizers is also within the scope of the invention. Zirconia partially stabilized by about 7 weight percent (about 4 molar percent) yttria is the most widely used TBC material because of its combination of low thermal conductivity, stability, good mechanical properties, and wear resistance, and therefore is believed to be a particularly suitable ceramic material for the ceramic coating 14 of the invention, though yttria contents of less than and greater than four molar percent are also within the scope of this invention. For use as a TBC, the thickness of the ceramic coating 14 will typically be in a range of about 250 micrometers to about 750 micrometers, with lesser and greater thicknesses also foreseeable.

[0023] According to a preferred aspect of the invention, the ceramic coating 14 is formed by a sol-gel, colloidal, or slurry-based process, by which a solution containing a precursor of the desired ceramic material for the coating 14 is applied to form at least one and preferably a plurality of precursor coating layers, which then undergo thermal processing to convert the precursor to the ceramic material. Particularly suitable precursors for the sol-gel process include, but are not limited to, acetylacetonate, oxychloride-hydroxyoxide, nitrate salt, and organometallic compounds. The precursor preferably contains a dispersion of ceramic particles, which remain dispersed in the ceramic coating 14 following thermal processing of the precursor coating layers. Previously, the thickness of a ceramic coating formed by a sol-gel process has been severely limited, often not more than about 10 micrometers, due to the tendency for the coating to crack and spall, as evidenced by FIGS. 3 through 5. Though not wishing to be held to any particular theory, the lack of robust attachment in the prior art sol-gel TBC of FIGS. 3 through 5 is believed to be primarily attributable to the colloidal particles being in suspension too far from the underlying substrate surface, and insufficient reactivity of the particles to form a strong bond with the surface.

[0024] The present invention is intended to enable the ceramic coating 14 to be adherent at thicknesses of at least 200 micrometers, and preferably at least about 500 micrometers or more, through the inclusion in the coating system of a ceramic film 20 that overlies the bond coat 16 and directly contacts the ceramic coating 14, as schematically represented in FIG. 1 (not to scale). The ceramic film 20 is preferably formed by a colloidal, slurry, or sol-gel based process, in which ceramic particles are dispersed in a precursor of a ceramic material, after which the resulting primer mixture is applied to the surface of the bond coat 16 to form a precursor primer layer. Particularly suitable precursors for colloidal and slurry-based processes include, but are not limited to, cellulose acetate, polyvinyl alcohol, polyvinyl chloride, acrylics, butyl alcohol, polyethyl oxides, polyvinyl propylene, phenolic resins, water-soluble resins, and alcohol-soluble resins.

The colloidal or slurry-based primer mixture can be applied in a variety of manners, for example, those typical of sol gel based coatings such as spraying, dipping, or brushing, after which the resulting precursor primer layer is heated to convert the precursor to form a matrix of the ceramic material containing the dispersed ceramic particles. Drastically improved adhesion of the ceramic coating 14 has been achieved if the particle size and thickness of the precursor primer layer and the thickness of the resulting ceramic film 20 are limited. The composition, reactivity, and surface morphology of the particles are also believed to be relevant. The composition and reactivity of the particles are believed to provide enhanced chemical bonding of the ceramic coating 14, likely as a result of an improved thermally-grown oxide scale 18. Furthermore, the degree and strength of the bond between the ceramic film 20 and the oxide scale 18, as well as the bond between the ceramic film 20 and ceramic coating 14, are believed to be controlled by the composition and thickness of the ceramic film 20.

[0025] The ceramic film 20 is physically distinguishable from the ceramic coating 14 and any layers that form the coating 14, even though the ceramic film 20 and coating 14 may be formed, and preferably are formed, to have the same predominant constituent. For example, both may contain more zirconia by molar percent than any other individual constituent, as is the case with zirconia at least partially stabilized with yttria, for example, about 4 to about 20 weight percent yttria. As a particular example, both the ceramic film 20 and the coating 14 may have ceramic matrices consisting of YSZ containing the same molar percent of yttria. Though their matrices are both predominantly zirconia, as represented in FIG. 2, the particles (not represented in FIG. 2) dispersed in the ceramic film 20 must differ from the particles dispersed in the coating 14 in order for the ceramic film 20 to promote the thermal growth of an oxide scale 18 that is capable of achieving adequate adhesion of the coating 14. This difference exists even if the ceramic film 20 and the first deposited layer of the coating 14 are both formed by sol-gel (colloid-based) processes, and even if the ceramic film 20 and coating 14 contain the same matrix material and/or particles of the same composition. Notably, attempts to promote the adhesion of a ceramic coating 14 formed using a colloid-based process (such as sol-gel) by simply reducing the thickness of the first deposited layer of the coating 14 have not resulted in adequate adhesion.

[0026] In view of the above, the invention arises from the determination that the ceramic film 20 must have a limited thickness, contain a matrix whose composition is the same as or otherwise compatible with the matrix material of the coating 14, and contain a dispersion of particles of a limited size and particular composition that enable the ceramic film 20 to bond well to the coating 14 and the underlying metallic surface (such as the bond coat 16).

[0027] The ability of the ceramic film 20 to enhance

bonding of a relatively thick ceramic coating to a metallic substrate has been demonstrated using YSZ as the composition for the matrices and particles of the ceramic coating 14 and ceramic film 20, though it is believed that other coating compositions will also benefit from the ceramic film 20. Superior adhesion resulting from the inclusion of the ceramic film 20 was demonstrated through increased thermal cycle life and tensile adhesion strength, for example, in comparison to the TBC coating of FIGS. 3 through 5, which was applied by a sol gel process but failed very early or prematurely in thermal cycle testing. In a series of tests performed with ceramic films 20 of various thicknesses, coating systems incorporating the ceramic film 20 exhibited increased thermal cycle performance as well as increased tensile adhesion, whereas coatings without the ceramic film 20 but otherwise identical in composition and construction did not demonstrate an acceptable tensile adhesion level and prematurely spalled during thermal cycling.

[0028] In an investigation leading to the present invention, thermal cycling (furnace cycle test, or FCT) and adhesion tests were performed on specimens produced to have coatings with and without ceramic films within the scope of this invention. The coating systems were deposited on buttons formed of either PtAl or NiAl intermetallic. The precursor solutions for the matrices of the ceramic coatings and (if present) the ceramic films were a sol-gel made up of a binder mixture of ethyl cellulose and terpineol combined with zirconium 2,4-pentanedionate and yttrium 2,4-pentanedionate as precursors for zirconia (ZrO_2) and yttria (Y_2O_3), respectively. YSZ particles were dispersed in each of the precursor solutions to form either a primer mixture or a coating mixture.

[0029] For the investigation, YSZ particles combined with the precursor solution to form the primer mixtures (which, after application and conversion, will form a ceramic film, such as the ceramic film 20 in FIG. 1) included YSZ containing about 4 molar percent yttria in amounts of about 5 to about 40 weight percent of the primer mixture. Median particle sizes (d_{50}) ranged from about 20 to about 150 nanometers, particle surface areas ranged from about 9 to about 20 m^2/g , and particle crystalline size ranged from about 5 to about 50 nanometers. The particles for the primer mixtures (and, therefore, the precursor primer layer and the resulting ceramic film) were selected for their small primary particle size, low crystallinity and high reactivity (attributed to surface area and crystalline size), which was theorized to promote sinterability of the particles and promote a more robust attachment to a thermally grown oxide (TGO) scale on the button specimens.

[0030] YSZ particles combined with the precursor solution to form coating mixtures for the investigation (and, after application and conversion, will form individual ceramic layers that in combination define a ceramic coating, such as the ceramic coating 14 in FIG. 1) included YSZ containing about 4 molar percent yttria in amounts of about 10 to about 40 weight percent of the coating mix-

ture. Median particle sizes (d50) ranged from about 50 nanometers to about 10 micrometers, and particle surface areas ranged from about 11 to about 117 m²/g. In comparison to the particles for the primer mixtures described above, the particles of the coating mixtures (and, therefore, the precursor coating layers and the resulting ceramic coating) were selected to be of lower reactivity and lower sinterability, which was theorized would control shrinkage and reduce delamination during conversion of the precursor coating layers to ceramic coating layers.

[0031] Prior to application of the primer and coating mixtures, the buttons were subjected to a two-hour oxidation treatment to develop an alumina scale having a thickness of about 100 to about 250 nanometers. On buttons intended to have a ceramic film incorporated into their coating systems, the primer mixtures were deposited on each button by spraying to form a single layer having a thickness of about 4 to about 20 micrometers. On all buttons, the coating mixtures were deposited by spraying to form multiple layers, each having a thickness of about 6 to about 12 micrometers. Depending on the coating, one or more curing treatments were performed at a temperature of about 150°C for a duration of about fifteen minutes to eliminate the solvent and cure the binder in the primer and coating mixtures, yielding individual precursor coating layers built up directly on the oxidized surfaces of button specimens that were not coated with the primer mixture, and individual precursor coating layers built up directly on the surfaces of the precursor primer layers of button specimens that were coated with the primer mixture. Thereafter, the buttons were subjected to thermal treatments at about 1000°C to burn off the binder and convert the precursors, yielding ceramic coating layers (formed from the precursor coating layers) and, if present, ceramic films (formed from the precursor primer layers) having essentially identical YSZ matrices containing a dispersion of their respective YSZ particles. The resulting ceramic films had thicknesses of about 4 to about 20 micrometers, the individual ceramic coating layers had thicknesses of about 6 to about 12 micrometers, and in combination the individual ceramic coating layers formed ceramic coatings having thicknesses of about 100 to about 500 micrometers.

[0032] The test conditions of the thermal cycling investigation included one-hour cycles between room temperature and about 2000°F (about 1090°C). Individual buttons were removed from thermal cycling once its coating system had sustained about twenty percent spallation. The adhesion strengths of the coating systems (normal to the surface of the buttons) were measured using known tensile adhesion testing techniques, in which an increasing tensile load was applied until tensile fracture occurred.

[0033] Selected test specimens and results from the investigation are summarized in Tables I, II and III of FIGS. 9, 10 and 11. In Tables I, II and III, Tosoh 4YM-1 and Tosoh 4YM identify powders of zirconia stabilized by about four molar percent yttria (hereinafter, M%YSZ

is used to indicate yttria contents in molar percent). The powders were obtained from the Tosoh Corporation, had a primary crystal size of about 25 nm, and were milled to obtain a mean particle size (d50) of about 60 nm. Also in Tables I, II and III, Unitec 4Y is a 4M%YSZ powder commercially-available from Unitec Ceramics, Ltd. under the designation Unitec-0001H (primary crystal size of about 12 nm, mean particle size (d50) of about 250 nm), MELox 3Y is a 3M%YSZ powder commercially-available from MEL Chemicals, Inc., (primary crystal size of about 62 nm, mean particle size (d50) of about 250 nm), and Tosoh 4Y Calcined is the aforementioned Tosoh 4YM after heat treatment at about 1100°C calcine as a loose powder to partially sinter the particles. V-0006 is a commercial polymeric binder system. The number of layers listed in Tables I, II and III indicate the number of layers deposited prior to a curing step, each layer being formed by a single spray pass. As noted above, after deposition all samples were processed at about 1000°C to burn off the binders and convert the precursor primer and coating layers.

[0034] The data in Tables I and II evidence that FCT lives were improved by a factor of about two to about four by the presence of a ceramic film incorporated into the coating system (Table II), in comparison to those coating systems lacking a ceramic film (Table I). Furthermore, ceramic films exceeding thirty micrometers in thickness (not represented in the Tables) fractured as a result of volumetric shrinkage during firing, resulting in spallation of their overlying ceramic coatings during FCT testing. FIGS. 6 and 7 exemplify one of the coating systems produced and tested during the investigation. The coating system has a thick ceramic coating (about 150 micrometers) overlying a thin ceramic film (about 8 micrometers). The ceramic coating (corresponding to the ceramic coating 14 in FIG. 1) has a YSZ matrix containing about 30 weight percent of the Unitec-001H YSZ particles with a median particle size (d50) of about 50 to about 250 nanometers, and particle surface area of about 40 to about 100 m²/g. The ceramic film (corresponding to the ceramic film 20 in FIG. 1) has the same YSZ matrix as the ceramic coating, but contained about 20 weight percent of the Tosoh 4YM YSZ particles with a median particle size (d50) of about 40 to about 70 nanometers, and particle surface area of about 15 to about 20 m²/g. In the as-deposited and fired condition shown in FIGS. 6 and 7, the ceramic coating can be seen to be crack-free and well adhered to the ceramic film, which is in stark contrast to the prior art coating system of FIGS. 3 and 4. When subjected to the thermal cycling test, this coating was crack-free and well-adhered when it was sectioned after completing 100 thermal cycles, as evidenced by FIG. 8. Such results are again in contrast to the prior art coating system shown in FIG. 5.

[0035] From the results of the investigation, it was concluded that the composition, reactivity, size, and surface morphology of the particles in the ceramic film 20 and the thickness of the ceramic film 20 must be carefully

controlled to enable a ceramic coating 14 of at least 500 micrometers thickness to be crack-free and well adhered in the as-deposited condition and exhibit acceptable thermal cycling and adhesion properties. In particular, it was concluded that ceramic particles within the ceramic film 20 preferably have a median particle size (d₅₀) of about 20 to about 100 nanometers, more preferably about 50 to about 100 nanometers. In the precursor primer layer, the particles preferably constitute about 10 to about 40 weight percent, and in the ceramic film 20 the particles preferably constitute about 15 to about 30 weight percent, more preferably about 20 to about 25 weight percent. Furthermore, it was concluded that the precursor primer layer should be deposited to a thickness of not more than 30 micrometers, preferably not more than 20 micrometers, and more preferably about 4 to about 20 micrometers, to yield a ceramic film having a thickness of not more than 30 micrometers, preferably not more than 20 micrometers, and more preferably about 4 to about 20 micrometers. If these limitations are met, a crack-free and well-adhered ceramic coating 14 can be formed by depositing a sol-gel or other suitable colloid-based coating mixture to have a thickness of greater than the precursor primer layer to yield a ceramic coating 14 having a thickness of greater than the ceramic film. For use as a TBC, preferred materials for the ceramic matrices and particles of the ceramic coating 14 and film 20 include YSZ, particularly YSZ containing about 4 molar percent yttria, and the thickness of the ceramic coating 14 will typically be at least 200 micrometers, such as in a range of about 250 up to about 750 micrometers and, in some cases, more preferably about 250 to about 500 micrometers.

[0036] While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art. Therefore, the scope of the invention is to be limited only by the following claims.

Claims

1. A process of forming a coating system on a component, the process comprising:

forming a precursor primer layer on and contacting a surface region of the component, the precursor primer layer having a thickness of up to 30 micrometers and comprising a precursor of a first ceramic material having a predominant constituent and a dispersion of particles of the first ceramic material, the particles having a median particle size of about 20 to about 100 nanometers;

forming at least a precursor coating layer on and contacting the precursor primer layer, the precursor coating layer having a thickness of greater than the precursor primer layer and comprising a precursor of a second ceramic material

having the same predominant constituent as the first ceramic material and a dispersion of particles of the second ceramic material; and then heating the precursor primer layer and the precursor coating layer to form a ceramic film from the precursor primer layer and a ceramic coating layer from the precursor coating layer, the ceramic film having a thickness of up to 30 micrometers and consisting essentially of the particles of the first ceramic material in a matrix of the first ceramic material, the ceramic coating layer having a thickness of greater than the ceramic film and consisting essentially of the particles of the second ceramic material in a matrix of the second ceramic material.

2. The process according to claim 1, wherein at least one of the precursor primer layer and the precursor coating layer is formed by applying a colloid or slurry.
3. The process according to claim 2, wherein the colloid or slurry comprises at least one of cellulose acetate, polyvinyl alcohol, polyvinyl chloride, acrylics, butyl alcohol, polyethyl oxides, polyvinyl propylene, phenolic resins, water-soluble resins, and alcohol-soluble resins.
4. The process according to claim 1, wherein the precursor coating layer is formed by applying a sol-gel.
5. The process according to claim 4, wherein the sol-gel comprises at least one of acetylacetonate, oxychloride-hydroxyoxide, nitrate salt, and organometallic compounds.
6. The process according to any preceding claim, wherein the first and second ceramic materials consist essentially of zirconia stabilized by yttria.
7. The process according to any preceding claim, wherein the ceramic film has a thickness of up to about twenty micrometers.
8. The process according to claim 1, wherein the ceramic film has a thickness of about four to about twenty micrometers.
9. The process according to any preceding claim, further comprising forming a plurality of additional precursor layers on the precursor coating layer, the additional precursor layers having a combined thickness of greater than the precursor coating layer and comprising the precursor of the second ceramic material and a dispersion of particles of the second ceramic material, wherein the heating step causes the additional precursor layers to form additional ceramic layers consisting essentially of the second ceramic material, the ceramic coating layer and the additional

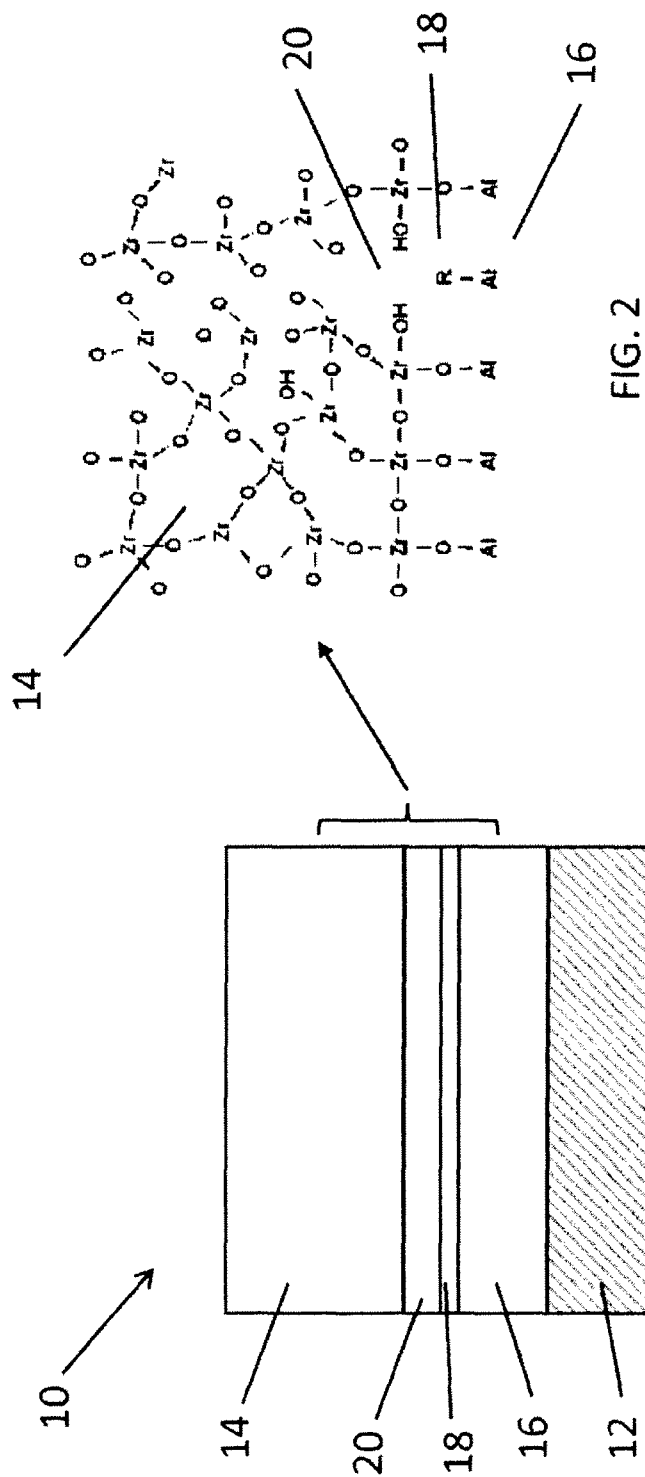
ceramic layers having a combined thickness of at least 200 micrometers.

10. The process according to any preceding claim, wherein the surface region on the component comprises a metallic bond coat on the component. 5
11. The process according to claim 10, wherein the surface region further comprises an oxide scale on the metallic bond coat, and the precursor primer layer is deposited on and contacts the oxide scale. 10
12. The process according to claim 11, wherein the metallic bond coat contains aluminum and the oxide scale comprises alumina. 15
13. The process according to any preceding claim, wherein the component is a gas turbine engine component formed of a nickel-base or cobalt-base superalloy. 20
14. The process according to claim 1 of forming a coating system on a gas turbine engine component, the process comprising: 25
forming on the component a metallic bond coat of predominantly an aluminide intermetallic;
forming an oxide scale on the metallic bond coat;
applying a colloid or slurry to form a precursor primer layer on and contacting the oxide scale, the precursor primer layer having a thickness of up to 30 micrometers and comprising a precursor of a first ceramic material having a predominant constituent and a dispersion of particles of the first ceramic material, the particles having a median particle size of about 50 to about 100 nanometers and constituting about 10 to about 40 weight percent of the precursor primer layer; 30
applying a sol-gel to form a first precursor coating layer on and contacting the precursor primer layer, the first precursor coating layer having a thickness of greater than the precursor primer layer and comprising a precursor of a second ceramic material having the same predominant constituent as the first ceramic material and a dispersion of particles of the second ceramic material; 35
applying a sol-gel to form a plurality of additional precursor coating layers on the first precursor coating layer, the additional precursor coating layers having a combined thickness of greater than the first precursor coating layer and comprising the precursor of the second ceramic material and a dispersion of particles of the second ceramic material; and then 40
heating the precursor primer layer and the first and additional precursor coating layers to form a ceramic film from the precursor primer layer 45
50
55

and a ceramic coating from the first and additional precursor coating layers, the ceramic film having a thickness of up to 30 micrometers and consisting essentially of the particles of the first ceramic material in a matrix of the first ceramic material, the ceramic coating having a thickness of greater than 200 micrometers and consisting essentially of the particles of the second ceramic material in a matrix of the second ceramic material.

15. A coating system on a surface region of a component, the coating system comprising:

a ceramic film on and contacting the surface region, the ceramic film having a thickness of up to 30 micrometers and consisting essentially of a first matrix of a first ceramic material having a predominant constituent and a dispersion of particles of the first ceramic material; and
a ceramic coating on and contacting the ceramic film, the ceramic coating having a thickness of greater than 200 micrometers and consisting essentially of a second matrix of a second ceramic material and a dispersion of particles of the second ceramic material, wherein the second ceramic material has the same predominant constituent as the first ceramic material.



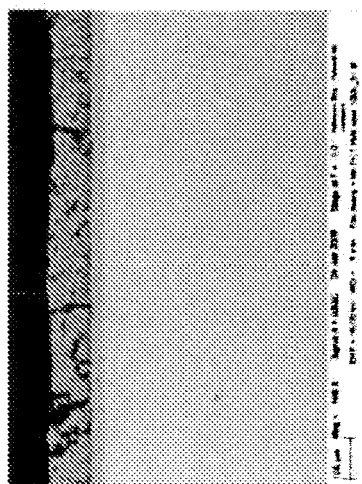


FIG. 3 (Prior Art)

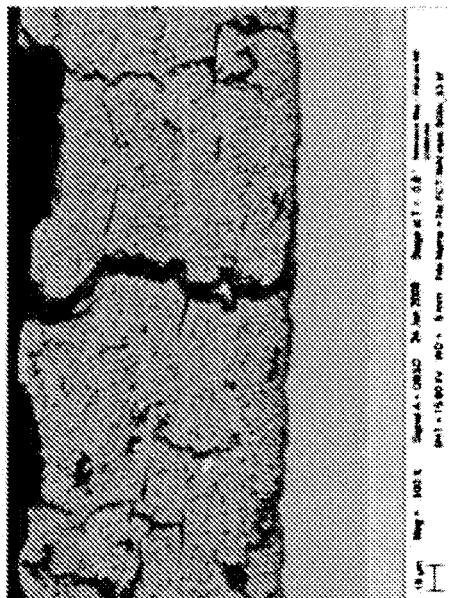


FIG. 4 (Prior Art)

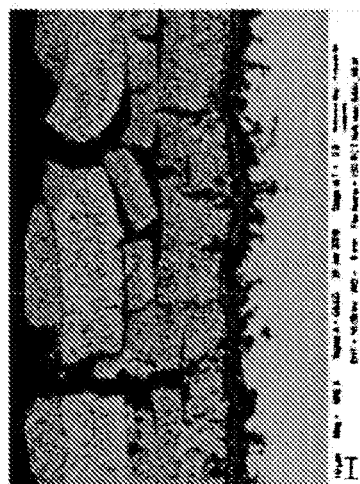


FIG. 5 (Prior Art)

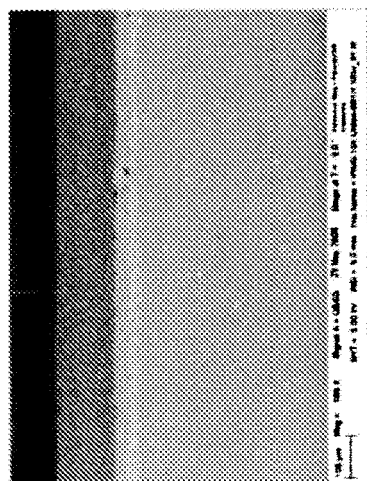


FIG. 6

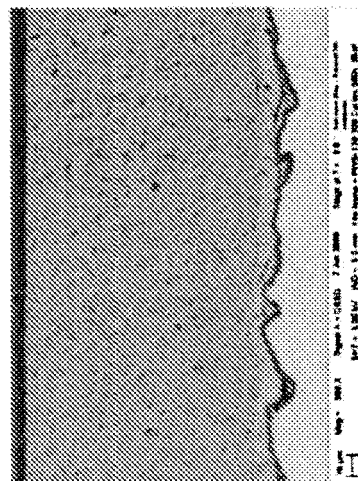


FIG. 8

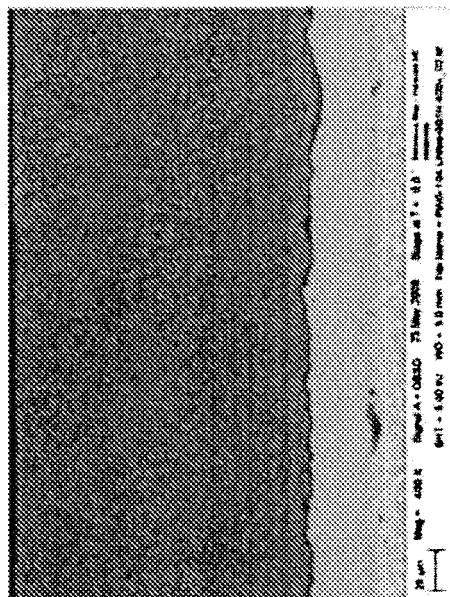


FIG. 7

TABLE I: Without Primer Layer; Thermal Cycle Data

Sample	Coating description			Thickness Total (μm)	FCT (cycles)
	Particle Material	# Layers	Loading		
# 18 (2)	Unitec 4Y	4	33 wt %	50	3
# 20 (2)	MELOx 3Y	4	33 wt %	50	38
# 7 (3)	Tosoh 4YM	5	33 wt %	75	120
			AVG	58	53.67
			Std. Dev.	13	60.5
# 35	Tosoh 4YM-1	4+4	30 wt%	75	100
# 32	Tosoh 4YM	4	33 wt%	38	196
# 33	Tosoh 4YM	4	33 wt%	38	296
			AVG	50	197
			Std. Dev.	22	98.01

FIG. 9

TABLE II: With Primer Layer; Thermal Cycle Data

Sample	Coating description			Thickness (μm)		FCT (cycles)	
	Particle Material	# Layers	Loading	Film	Total		
# 66	Tosoh 4YM	1	33 wt%	8-12	148	395	
	Unitec 4Y	5+5+5	33 wt%				
# 67	Tosoh 4YM	1	33 wt%	8-12	154	395	
	Unitec 4Y	5+5+5	33 wt%				
# 68	Tosoh 4YM	1	33 wt%	8-12	160	315	
	Unitec 4Y	5+5+5	33 wt%				
AVG					154	368.33	
Std. Dev.					6	46.19	
# 72	Tosoh 4YM	1	33 wt%	8-12	125	180	
	MELox 3Y	5+5+5	33 wt%				
# 73	Tosoh 4YM	1	33 wt%	8-12	128	560	
	MELox 3Y	5+5+5	33 wt%				
# 74	Tosoh 4YM	1	33 wt%	8-12	130	560	
	MELox 3Y	5+5+5	33 wt%				
AVG					128	433	
Std. Dev.					3	219.39	

FIG. 10

TABLE III: With Primer Layer; Adhesion Data

Sample	Coating description			Thickness (μm)		Adhesion (psi)
	Particle Material	# Layers	Loading	Film	Total	
# 127	Tosoh 4YM	1	33 wt%	8-12	150	1530
	Unitec 4Y	5+5+5	33 wt%			
# 128	Tosoh 4YM	1	33 wt%	8-12	144	1306
	Unitec 4Y	5+5+5	33 wt%			
# 129	Tosoh 4YM	1	33 wt%	8-12	163	1264
	Unitec 4Y	5+5+5	33 wt%			
AVG					152	1366.67
Std. Dev.					10	143.00
# 139	Tosoh 4YM	1	33 wt%	8-12	156	1543
	Tosoh 4Y Calcined	5+5+5	33 wt%			
# 140	Tosoh 4YM	1	33 wt%	8-12	146	1130
	Tosoh 4Y Calcined	5+5+5	33 wt%			
# 141	Tosoh 4YM	1	33 wt%	8-12	142	1657
	Tosoh 4Y Calcined	5+5+5	33 wt%			
AVG					148	1443.33
Std. Dev.					7	277.28
# 151	Tosoh 4YM	1	33 wt%	8-12	162	1359
	MELox 3Y	5+5+5	33 wt%			
# 152	Tosoh 4YM	1	33 wt%	8-12	158	1469
	MELox 3Y	5+5+5	33 wt%			
# 153	Tosoh 4YM	1	33 wt%	8-12	164	1406
	MELox 3Y	5+5+5	33 wt%			
AVG					161	1411
Std. Dev.					3	55.19

FIG. 11