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(54) **OPTIMIZED HIGH PURITY COATING FOR HIGH TEMPERATURE THERMAL CYCLING APPLICATIONS**

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(57) **ABSTRACT**

The invention is directed to a blended material and method for obtaining thermal barriers for high temperature cycling applications that have both high sintering resistance to achieve a high service lifetime and low thermal conductivity to achieve high operating temperatures. These materials are additionally suited for use in high temperature abradable (rub seal) coatings. The invention provides desired coating structures so that the changes in the coating microstructure over the in-service lifetime are either limited or beneficial.

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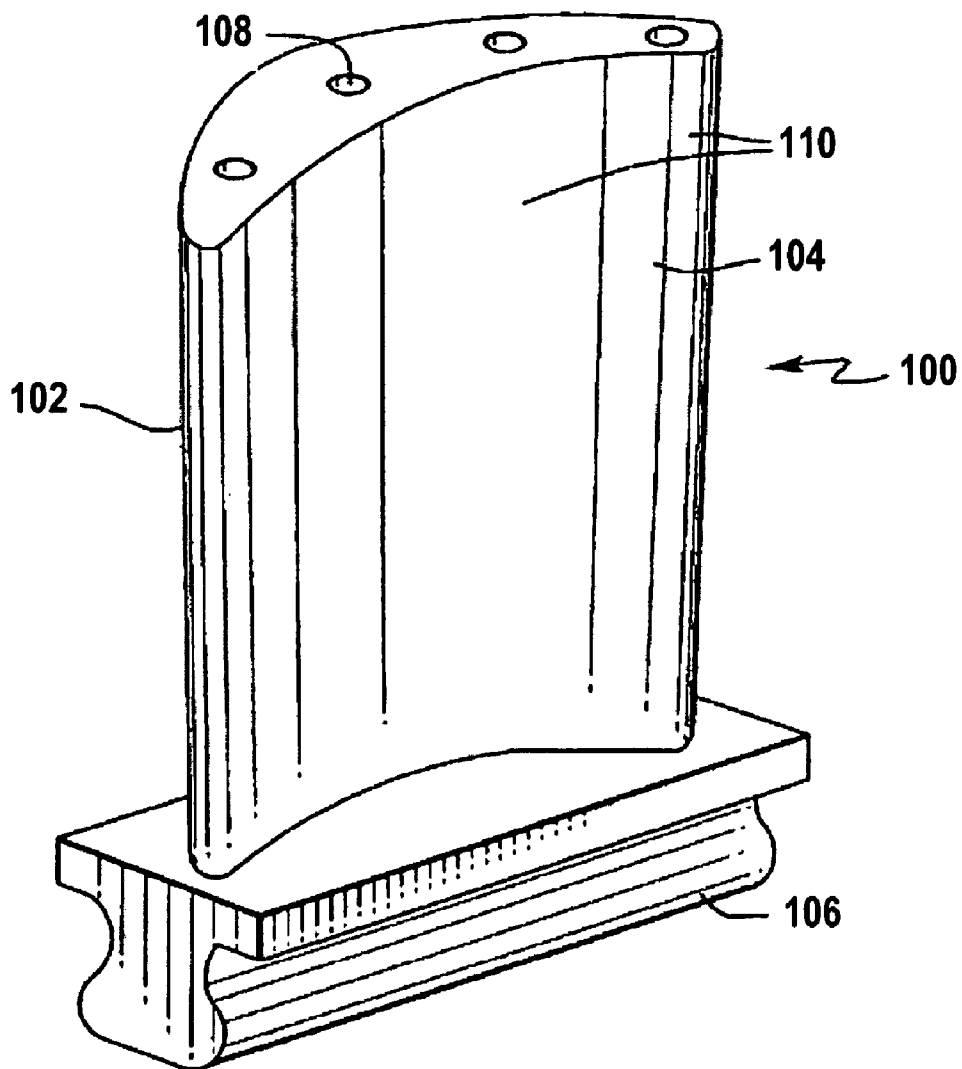


FIG. 1

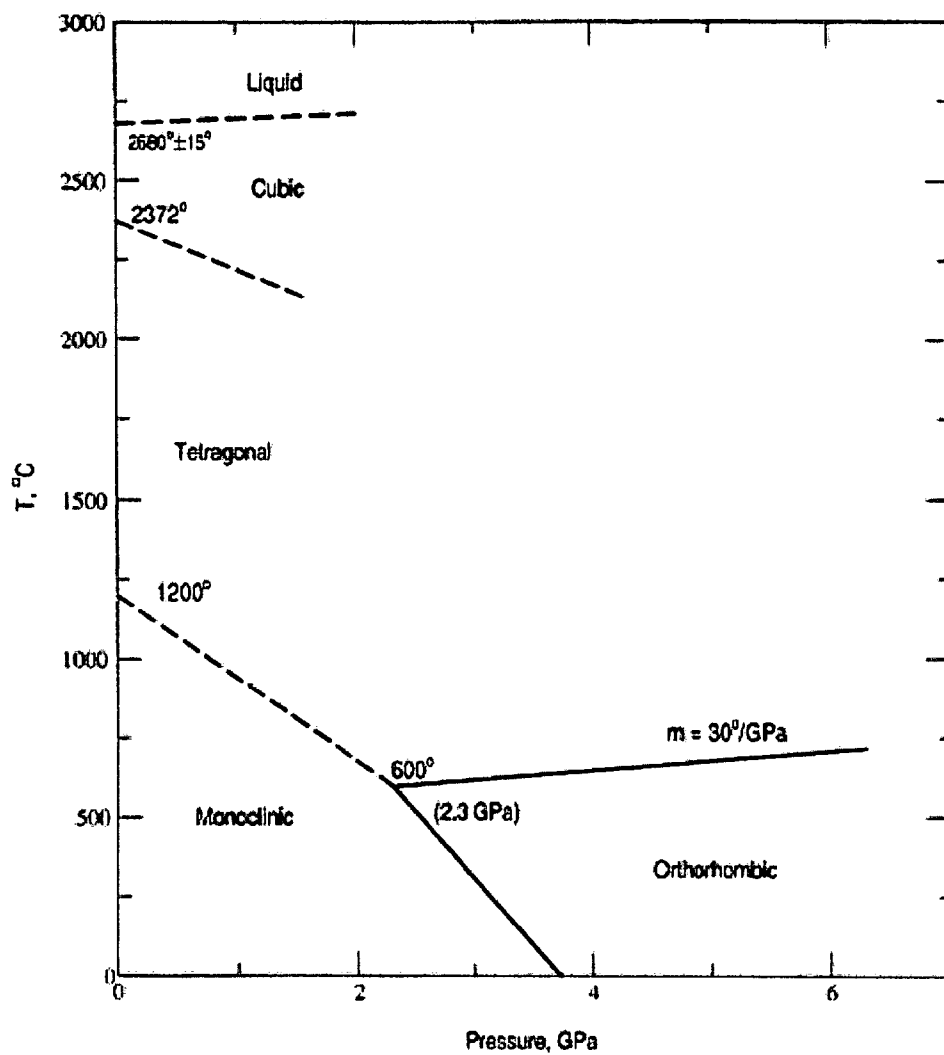


FIG. 2

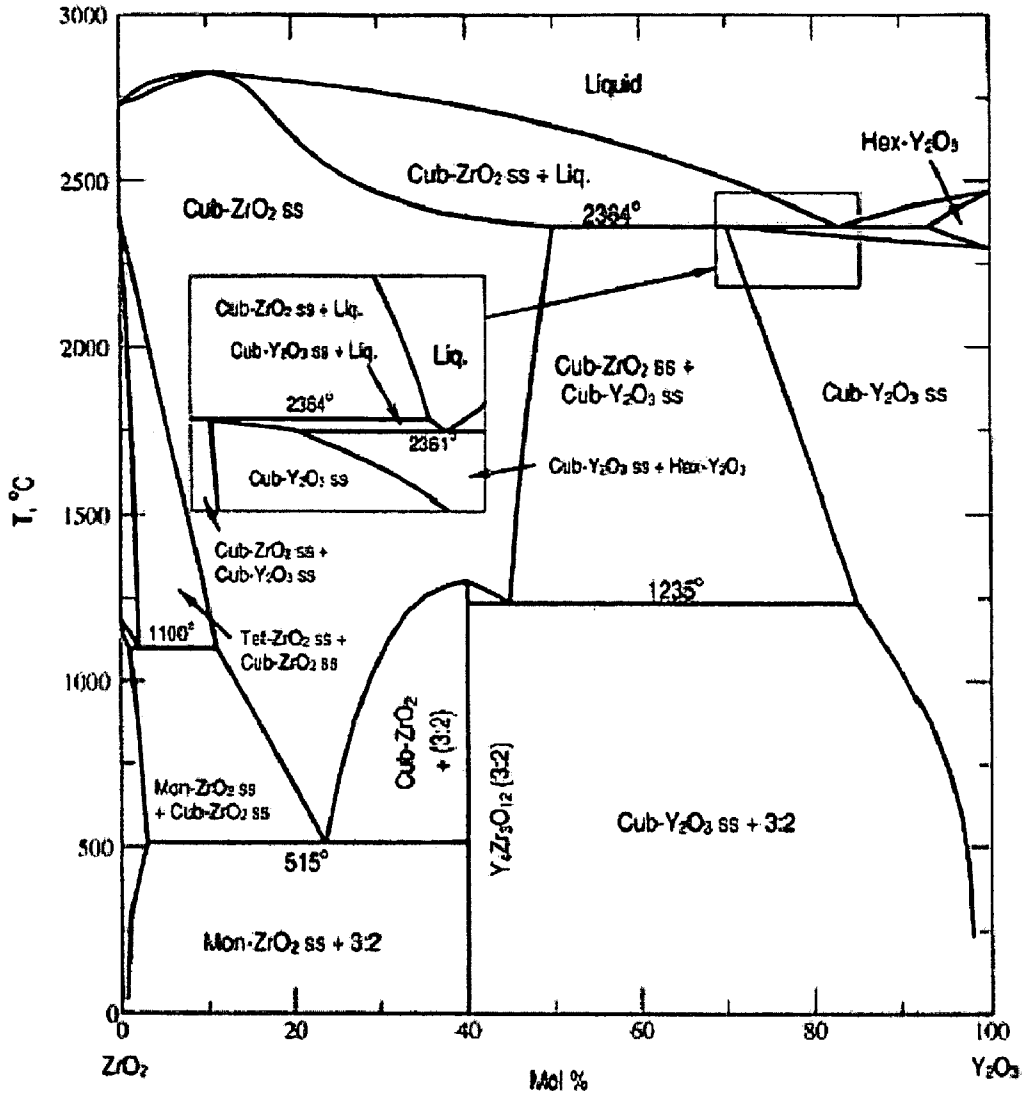


FIG. 3

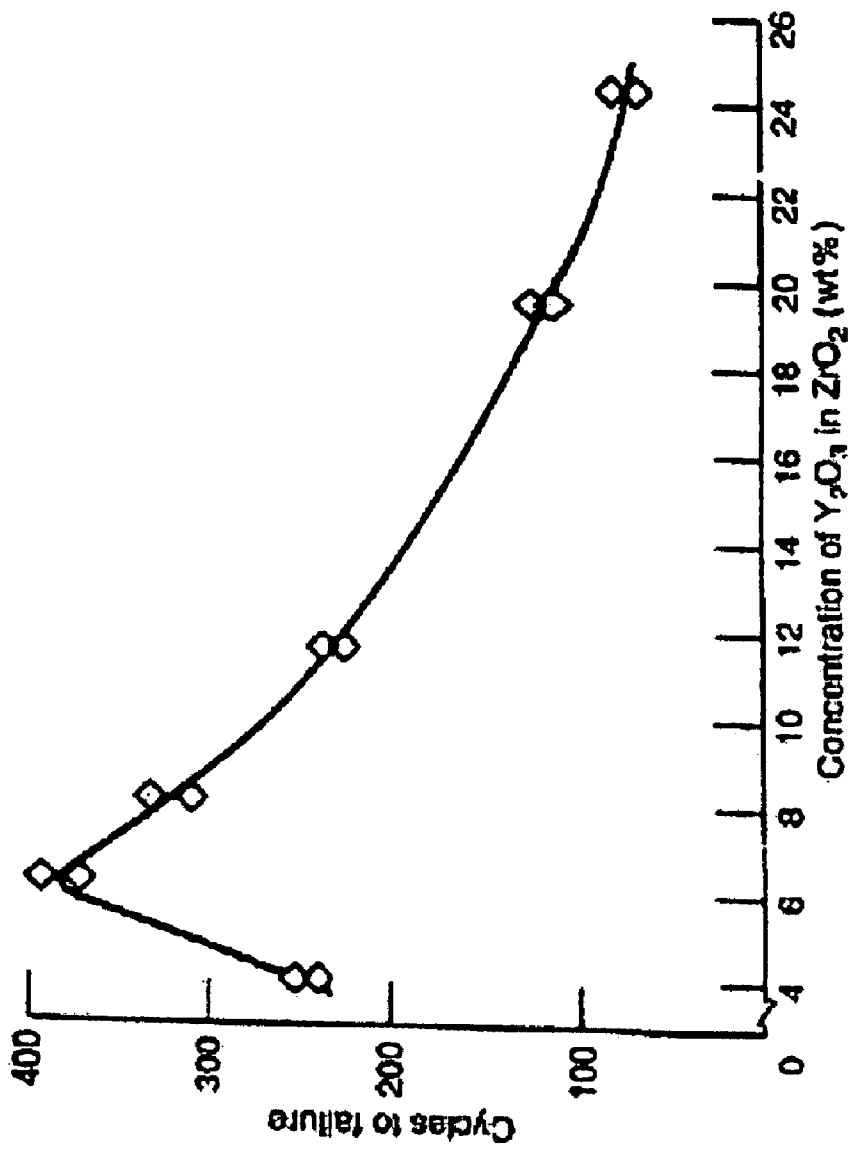


FIG. 4

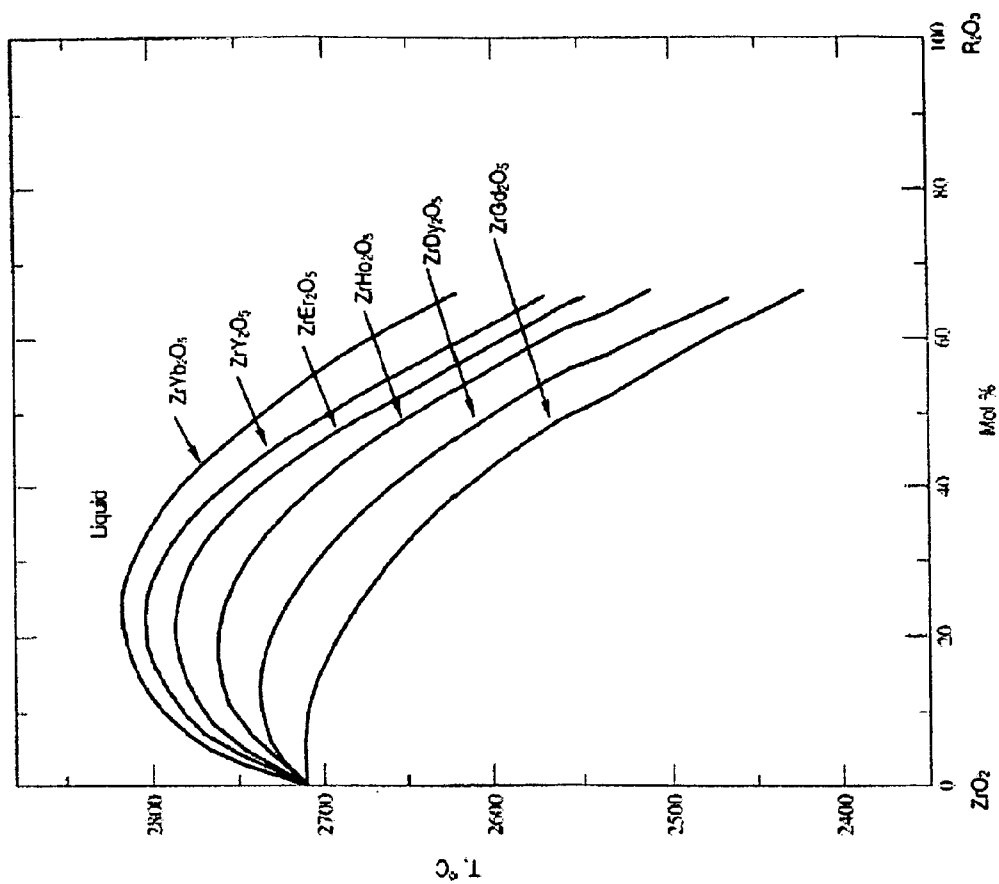


FIG. 5

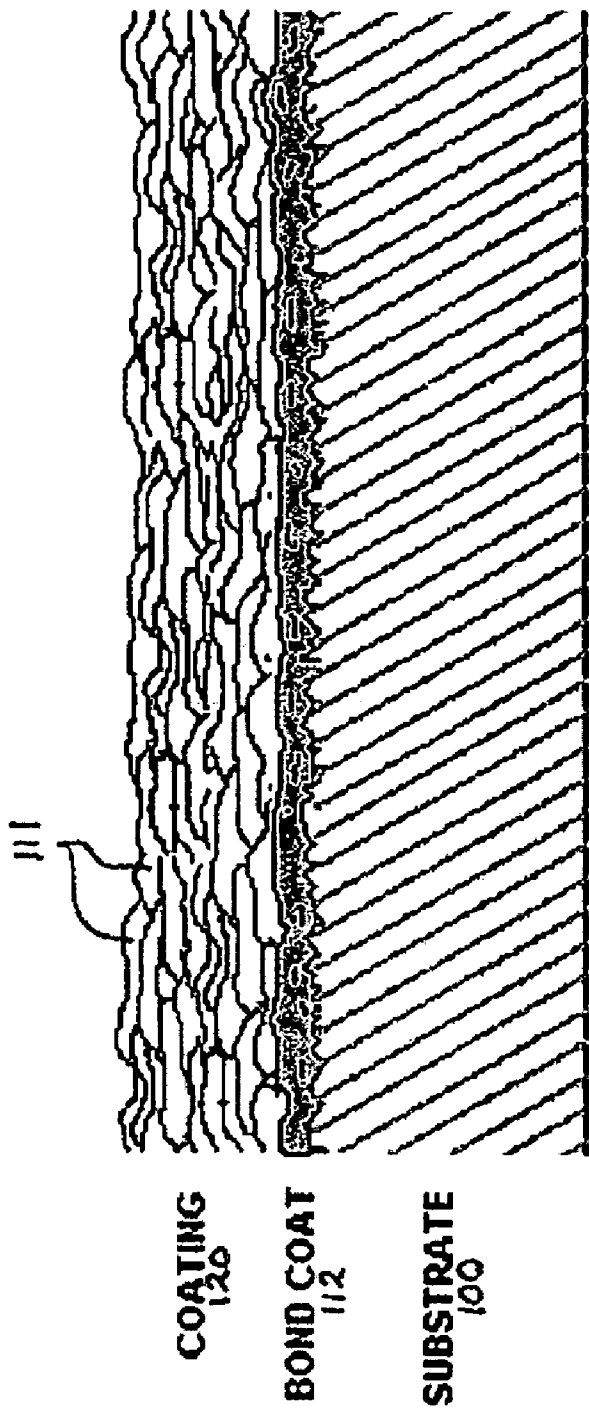


FIG. 6

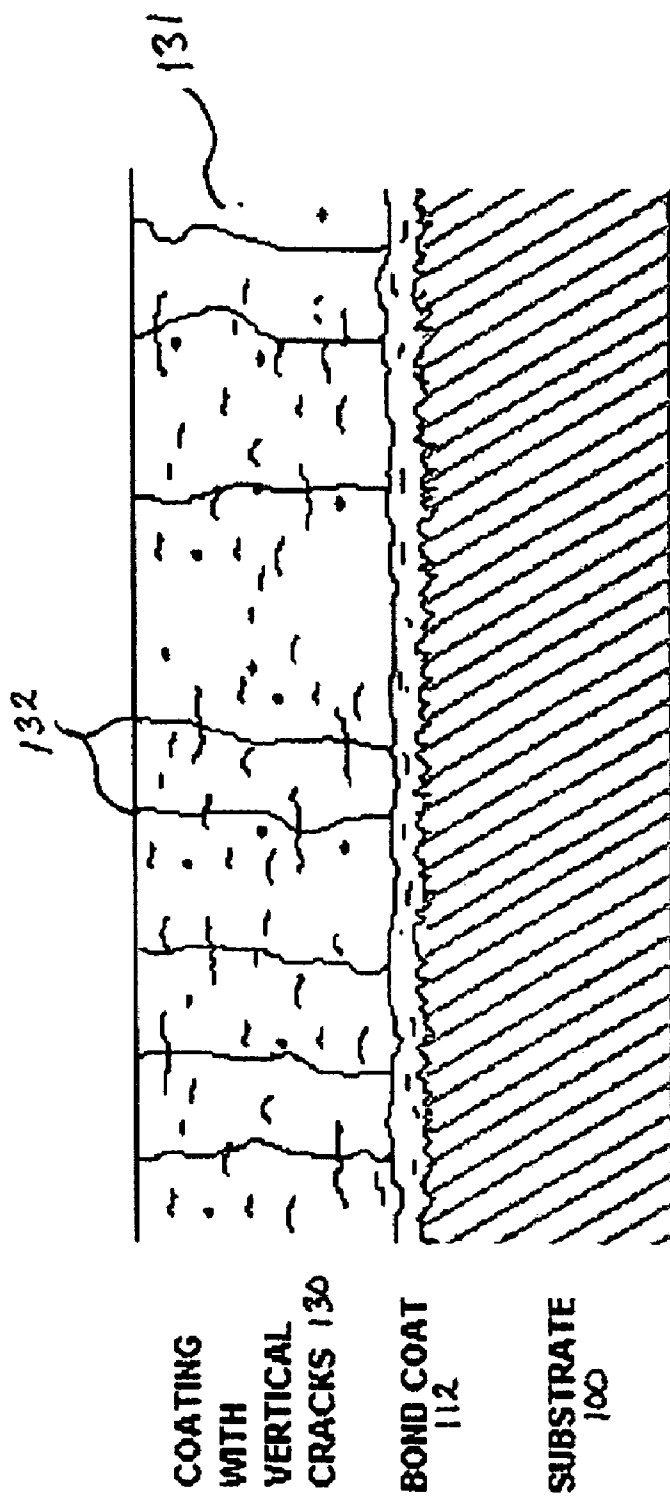


FIG. 7

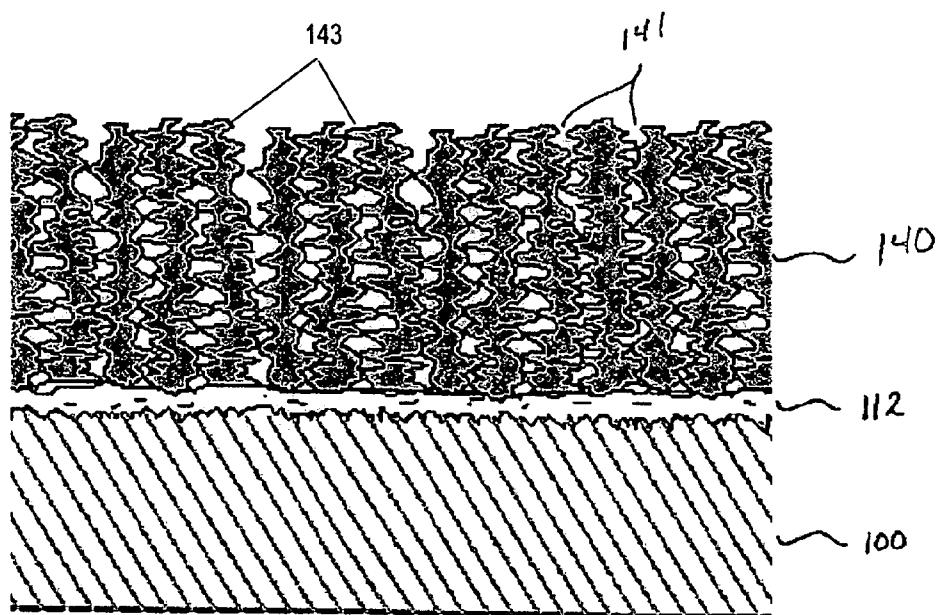


Figure 8: Structure of thermal barrier coating deposited from the vapor phase.

FIG. 8

THORNTON STRUCTURE ZONE MODEL
(For Sputtered Films)

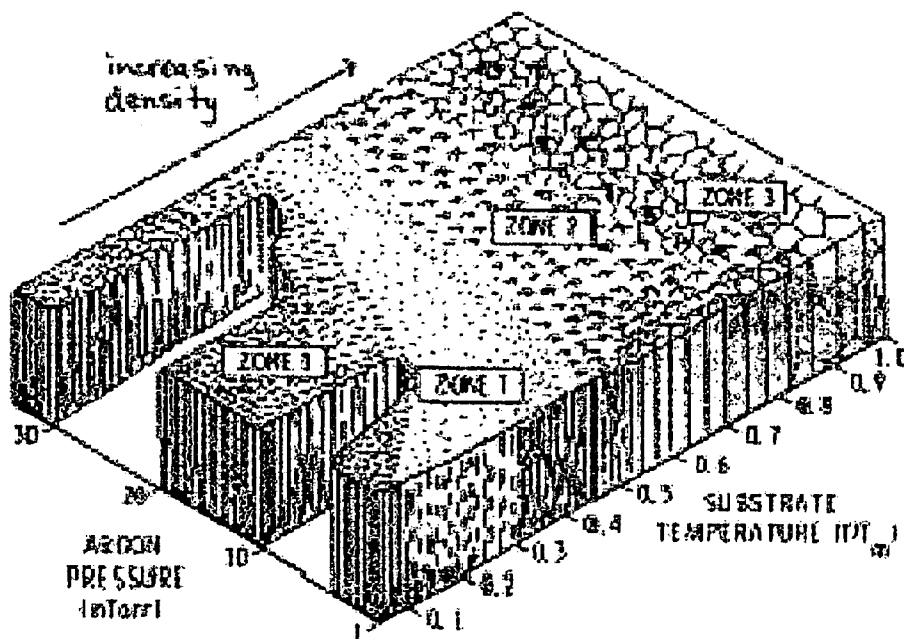


FIG. 9

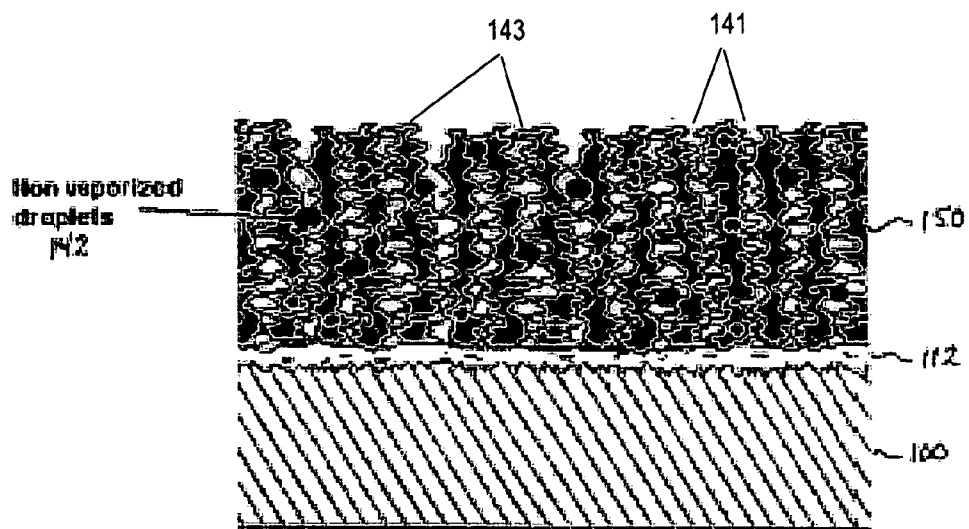


FIG. 10

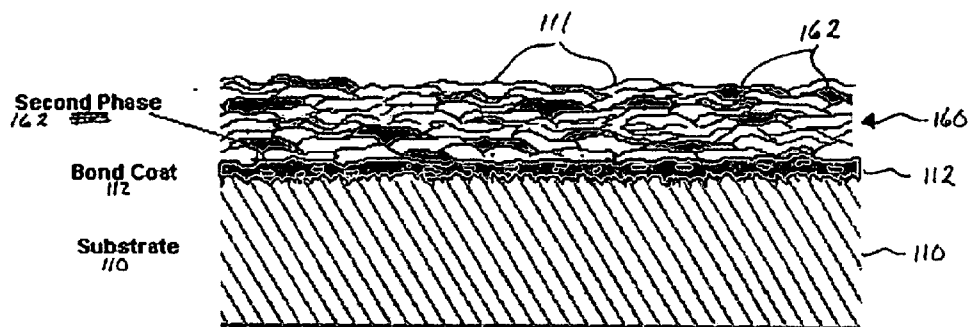


FIG. 11A

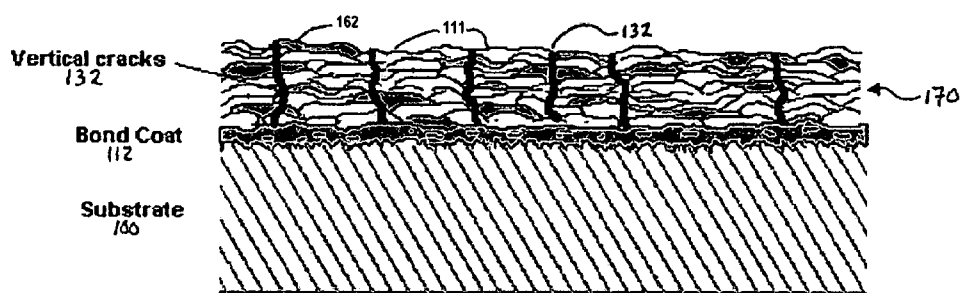


FIG. 11B

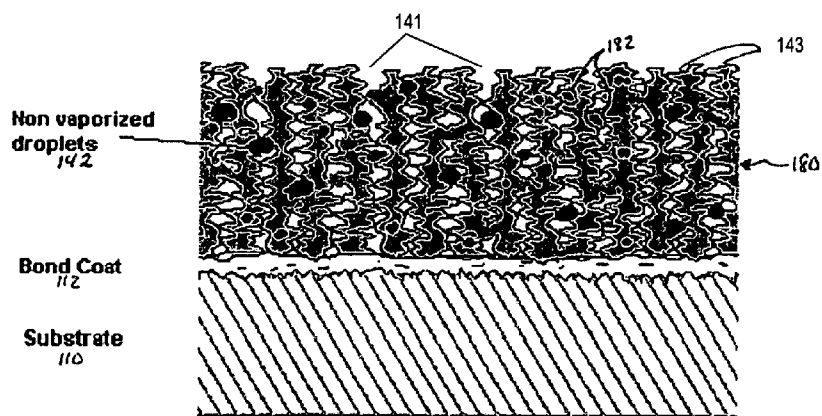


FIG. 11C

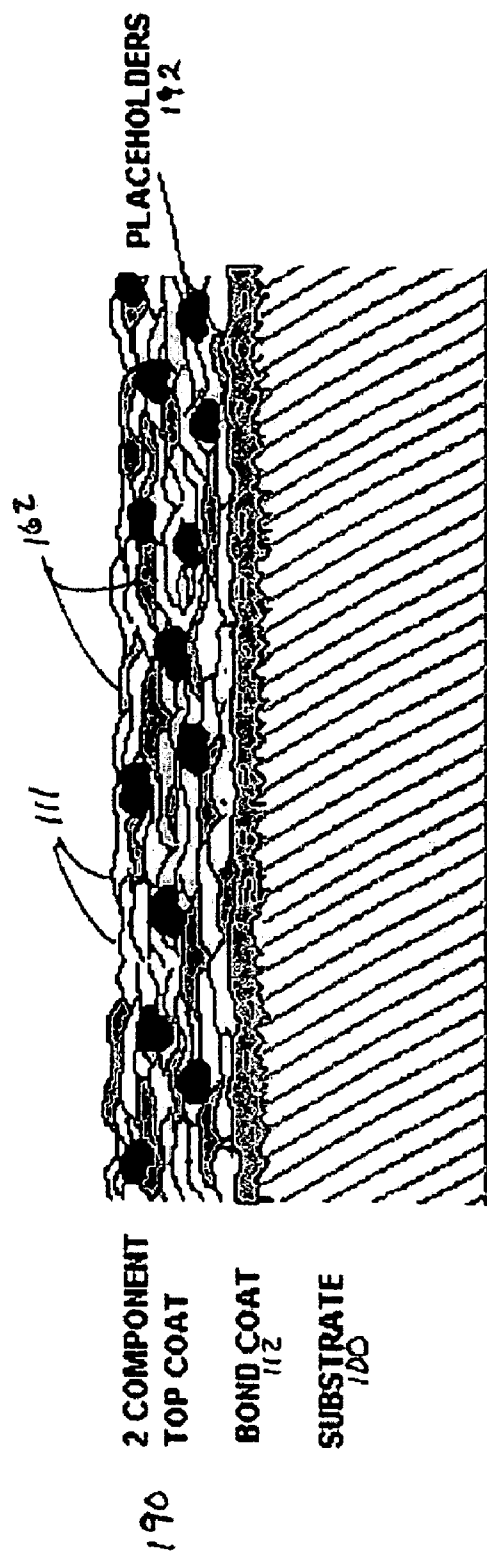


FIG. 12

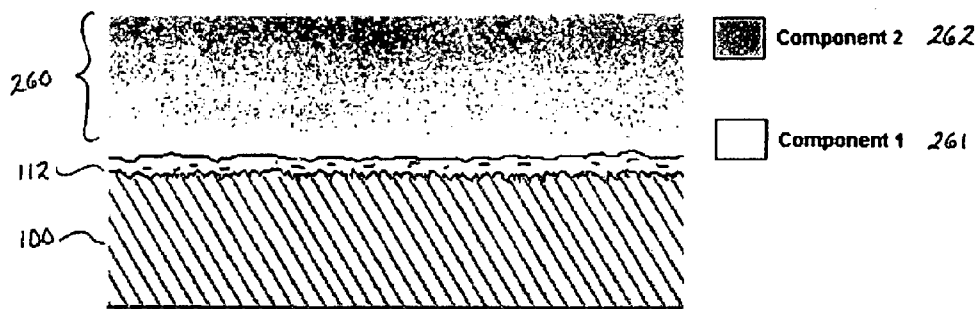


FIG. 13

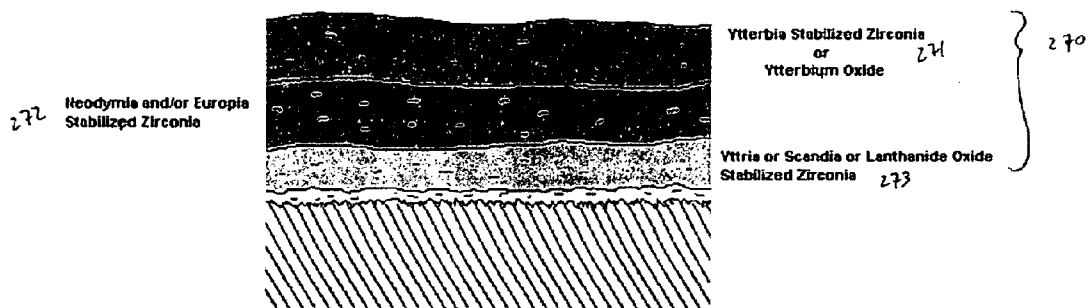


FIG. 14

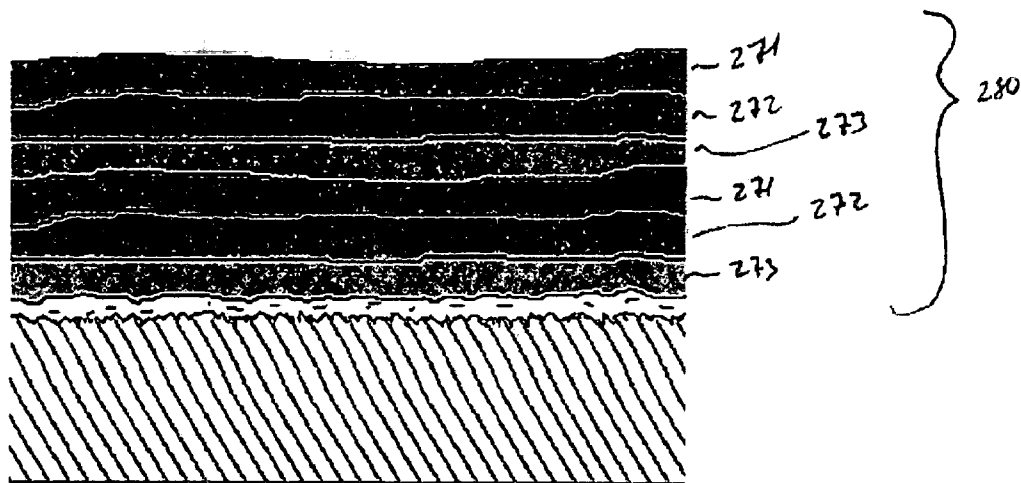


FIG. 15

OPTIMIZED HIGH PURITY COATING FOR HIGH TEMPERATURE THERMAL CYCLING APPLICATIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119(e) from U.S. Provisional Patent Application No. 60/724, 286, filed on Oct. 7, 2005, which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

REFERENCE TO A "MICROFICHE APPENDIX"

[0003] Not Applicable

BACKGROUND OF THE INVENTION

[0004] 1. Field of the Invention

[0005] The invention relates to ceramic materials for thermal barriers and abradable coating systems in high temperature and high temperature cycling applications, and more particularly to ultra-pure zirconia and/or hafnia materials for use in thermal barrier and abradable coating applications.

[0006] 2. Description of the Related Art

[0007] Superior high-temperature properties are required to improve the performance of heat resistant and corrosion resistant members. These members include, for example gas turbine blades, combustor cans, ducting and nozzle guide vanes in combustion turbines and combined cycle power plants. Turbine blades are driven by hot gasses, and the efficiency of the gas turbine increases with the rise in operational temperature. The demand for continued improvement in efficiency has driven the system designers to specify increasingly higher turbine operating temperatures. Thus, there is a continuing need for materials that can achieve higher operational temperatures. An additional design criteria for gas turbines is increased operating time between maintenance and repairs, meaning longer lifetime of the materials used in these applications.

[0008] Thermal barrier coatings are used to insulate components, such as those in a gas turbine, operating at elevated temperatures. Thermal barriers allow increased operating temperature of gas turbines by protecting the coated part (or substrate) from direct exposure to the operating environment. An important consideration in the design of a thermal barrier is that the coating be a ceramic material having a crystalline structure containing beneficial cracks and voids, imparting strain tolerance. If there were no cracks in the coating, the thermal barrier would not function, because the differences in thermal expansion between the metal substrate system and the coating will cause interfacial stresses upon thermal cycling that are greater than the bond strength between them. By the creation of a crack network into the coating, a stress relief mechanism is introduced that allows the coating to survive numerous thermal cycles. Repeating crack networks are typically imparted into the coating on varying space scales by manipulating the thermodynamic and kinetic conditions of the manufacturing method, and different structures known to perform the coating task have

been optimized likewise. In addition to this, cracks are also formed during service, so the structure formed upon coating manufacture changes with time, depending on the starting material phases in the manufactured coating and thermal conditions during service. There remains a need in the art for a coating material, coating material manufacturing method and coating manufacturing method that address the changes in the coating microstructure during its service lifetime.

[0009] In an effort to meet this need for materials with higher temperature capabilities, certain ceramic materials have been developed. These ceramic materials are used to protect the part and form a barrier so as to increase the thermal gradient, thereby reducing the temperature of the substrate. For example, the ceramic material yttria stabilized zirconia (YSZ) has been commonly used as such a coating material. Materials with even lower thermal conductivity continue to be sought to serve as coatings.

[0010] Another design factor determining coating lifetime is the sintering rate of the coating. When the coating is cycled above half of its absolute melting temperature, the coating begins to sinter causing volume shrinkage. As the coating shrinks, the modulus increases, lowering the strain tolerance of the coating and it becomes detached. Decreasing the sintering rate of the thermal barrier slows down this failure mechanism. For high purity zirconia alloys, the onset of sintering commences at temperatures above 1000° C.

[0011] A major disadvantage brought about by using typical zirconia coating systems is that zirconia is transparent to radiation in the infrared range. As thermal barriers are sought for higher temperatures, zirconia becomes limited in its effectiveness. The main mechanism of heat transfer for zirconia changes from conduction to radiation at temperatures approaching 1500° C. Since zirconia is nearly transparent to the heat radiation (in the form of photons) above those temperatures, its main function as a heat barrier becomes reduced. Thus, there remains a need in the art for a zirconia-based thermal barrier material that remains optimized at temperatures from 1200° C. to above 1500° C.

SUMMARY

[0012] Accordingly, the invention is directed to blends of ceramic materials for use in thermal barriers for high temperature cycling applications and high temperature abradable coatings. The materials are alloys formed predominantly from ultra-pure stabilized zirconia (ZrO₂) and/or hafnia (HfO₂) alloys that have uncharacteristically high sintering resistance to achieve a high service lifetime. The invention provides the combinations of desired coating materials so that the changes in the coating microstructure over the in-service lifetime are retarded.

[0013] The limits for impurities discovered to decrease sintering rate and therefore increase service lifetime compared with impurity concentrations present in current materials when used as a coating and stabilized for example, with yttria, are disclosed herein. Oxide impurities are defined as materials which, when combined with each other or with zirconia and/or hafnia, form phases with melting points much lower than that of pure zirconia and/or hafnia, especially but not limited to soda (Na₂O), silica (SiO₂) and alumina (Al₂O₃).

[0014] One aspect of the invention is to provide a blend of ceramic materials for use in high-temperature thermal bar-

riers or abradable seal coatings that have reduced sintering rates in addition to photon blocking or scattering characteristics. One material comprises of zirconia and/or hafnia and ytterbia (Yb_2O_5) and/or yttria (Y_2O_3), having a total amount of impurities of less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The zirconia and/or hafnia is partially stabilized by the ytterbia and/or yttria, and the specific oxide impurity concentrations of the material do not exceed 0.1 weight percent soda, 0.05 weight percent silica, and 0.01 weight percent alumina and 0.05 weight percent titania and preferably 0.01 weight percent soda, 0.01 weight percent silica, and 0.01 weight percent alumina and 0.01 weight percent titania. Another material comprises of zirconia and/or hafnia and neodymia (Nd_2O_3) and/or europia (Eu_2O_3), having a total amount of impurities of less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The zirconia and/or hafnia is partially stabilized by the neodymia and/or europia, and the specific oxide impurity concentrations of the material do not exceed 0.1 weight percent soda, 0.05 weight percent silica, and 0.01 weight percent alumina and 0.05 weight percent titania and preferably 0.01 weight percent soda, 0.01 weight percent silica, and 0.01 weight percent alumina and 0.01 weight percent titania.

[0015] In one aspect of the invention, a blended high-purity coating that is suitable for high temperature cycling applications is provided. The coating includes a first material and at least a second material. The first material is essentially about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer. The second material is of a different composition than the first material, and is also about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer. The first and second materials are blended together in the coating, and the total amount of impurities in the coating is less than or equal to 0.15 weight percent.

[0016] In another aspect of the invention, a high-purity coating structure that is suitable for high temperature cycling applications is formed by a process of the following steps: providing a first material in a form suitable for use in thermal spraying applications, wherein said first material is about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in the first material is less than or equal to 0.15 weight percent; providing a second material of a different composition than the first material and in a form suitable for use in thermal spraying applications, said second material is about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in second material is less than or equal to 0.15 weight percent; and applying each of the materials onto a metal substrate so that the materials are blended in the coating.

[0017] In a further aspect of the invention, a method for producing a high-purity coating structure is provided. The method includes providing a first material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities is less than or equal to 0.15 weight percent. Another step of the method includes providing a second material of a different composition than the first material, said second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in second material is less than or equal to 0.15 weight percent. Yet another step of the method includes and applying said materials onto a metal substrate.

[0018] According to another aspect of the invention, a layered high-purity coating is provided. Each layer may contain different types of a high-purity zirconia- or hafnia-based material that is partially stabilized by one or more rare earth oxide. The total amount of impurities in each coating layer less than or equal to 0.15 weight percent.

[0019] According to different aspect of the invention, a graded high-purity coating is provided. The coating is formed from two or more materials each of a high-purity zirconia- or hafnia-based material that is partially stabilized by one or more rare earth oxide. The first and one or more second materials form a compositional gradient through the thickness of the coating, and the total amount of impurities in the coating is less than or equal to 0.15 weight percent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The accompanying drawings are included to provide further understanding of the invention and are incorporated in and constitute a part of this specification. The accompanying drawings illustrate embodiments of the invention and together with the description serve to explain the principles of the invention. In the figures:

[0021] FIG. 1 illustrates a perspective view of a turbine blade coated with a thermal barrier of ceramic material;

[0022] FIG. 2 provides a phase diagram for ZrO_2 ;

[0023] FIG. 3 provides a phase diagram for ZrO_2 with stabilizer;

[0024] FIG. 4 provides a chart of composition vs. thermal cycles to failure for yttria stabilized zirconia;

[0025] FIG. 5 provides a chart showing the melting point of ZrO_2 vs. amount of stabilizer;

[0026] FIG. 6 provides a diagram showing a lamellar thermal barrier coating structure containing porosity and micro cracks;

[0027] FIG. 7 provides a diagram showing a lamellar thermal barrier coating structure containing macro cracks, porosity and micro cracks;

[0028] FIG. 8 provides a diagram showing a structure of thermal barrier coating deposited from the vapor phase;

[0029] FIG. 9 provides a diagram showing the Thornton model for predicting structure of a coating formed from the gas phase;

[0030] FIG. 10 provides a diagram showing a structure of thermal barrier coating deposited from both vapor and liquid phase;

[0031] FIG. 11A provides a diagram showing a lamellar thermal barrier coating structure formed from a blend of components containing porosity and micro cracks;

[0032] FIG. 11B provides a diagram showing a dense solid thermal barrier coating structure formed from a blend of components, containing macro cracks, porosity and micro cracks;

[0033] FIG. 11C provides a diagram showing a columnar thermal barrier coating structure formed from a blend of components;

[0034] FIG. 12 provides a diagram showing a thermal barrier coating structure formed from a blend of components and a placeholder;

[0035] FIG. 13 provides a diagram showing a thermal barrier coating containing a compositional gradient;

[0036] FIG. 14 provides a diagram showing a thermal barrier coating containing layers each of a different composition; and

[0037] FIG. 15 provides a diagram showing a thermal barrier coating containing a series of layers each of a different composition.

DETAILED DESCRIPTION OF THE INVENTION

[0038] Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings.

[0039] In an exemplary use of a material of the invention, FIG. 1 shows one component of a turbine. Turbine blade 100 has a leading edge 102 and an airfoil section 104, against which hot combustion gases are directed during operation of the turbine, and which undergoes severe thermal stresses, oxidation and corrosion. A root end 106 of the blade anchors the blade 100. Venting passages 108 may be included through the blade 100 to allow cooling air to transfer heat from the blade 100. The blade 100 can be made from a high temperature resistant material. The surface of the blade 100 is coated with a thermal barrier coating 110 made of ultra-pure zirconia (ZrO_2) and/or hafnia (HfO_2) alloys in accordance with the invention. The thermal barrier coating 110 may be applied on a MCrAlY bonding layer with an alumina scale (not shown) applied between the blade surface and the coating 110. The coating 110 may be applied onto the bond coating surface through a variety of methods known in the art including thermal spray techniques such as powder flame spray and plasma spray and vapor deposition methods such as electron beam physical vapor deposition (EBPVD), high speed physical vapor deposition and low pressure plasma spraying (LPPS).

[0040] When applied, the coating 110 contains a crack network that allows it to survive numerous thermal cycles. As described in the above background section, the crack network is altered to a less desirable state by sintering and

temperature cycling during service. Thus the structure formed upon coating manufacture changes with time, the rate depending on the starting material phases and service conditions. Decreasing the sintering rate increases the amount of time before the closing of microcracks and creation of massive cracks, increasing coating lifetime.

[0041] One feature of using zirconia (ZrO_2)-based and/or hafnia (HfO_2)-based systems is that they have both a high coefficient of thermal expansion relative to other ceramics that is close to the coefficient of thermal expansion of the MCrAlY bond coat and the metal substrate system it protects. Also these material systems have a low thermal conductivity to give the highest level of thermal protection. Other ceramic systems do not possess both of these functions. Zirconia is currently a preferred system, primarily because of its comparatively lower cost. Hafnia offers equivalent or superior property advantages over zirconia, but has typically not been used in commercial applications due to its prohibitive cost. Nonetheless, hafnia is almost always present in zirconia due to the difficulty of their separation during mineral processing. While further discussion for convenience will address the zirconia-based system, the discussion below is also applicable to hafnia-based systems.

[0042] To achieve optimal performance, the material purity of the starting materials (zirconia and/or hafnia) must be as high as possible within economic reason. For the present invention the zirconia and/or hafnia must have impurities of less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 weight percent. The reason for this is that impurities such as silica and alumina and soda have a lower melting temperature than zirconia or hafnia and cause an increase in the sintering rate of the coating structure. The increased sintering rate is undesirable because any increase in sintering rate decreases the lifetime of the coating. Sintering decreases the surface area of the crack network within the coating, increasing the coating modulus over time until failure occurs.

[0043] In certain embodiments, the material of the present invention contains zirconia (ZrO_2) and/or hafnia (HfO_2) and partially stabilized by a primary stabilizing oxide such as ytterbia and/or yttria, and possibly secondary stabilizers such as scandia or a lanthanide oxide having a total amount of impurities of less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. For purposes of the present invention, oxide impurities can be defined as materials which when combined with each other or with zirconia form phases with melting points much lower than that of pure zirconia, especially but not limited to soda (Na_2O), silica (SiO_2), and alumina (Al_2O_3). Other known impurities include titania (TiO_2), hematite (Fe_2O_3), calcia (CaO), and magnesia (MgO). In accordance with the invention, the limits for known impurities in order to achieve a desirable sintering rate and therefore increase service lifetime when used as a coating are:

[0044] Na_2O —0.1 weight percent

[0045] SiO_2 —0.05 weight percent

[0046] Al_2O_3 —0.01 weight percent

[0047] TiO_2 —0.05 weight percent

[0048] Fe_2O_3 —0.05 weight percent

- [0049] CaO—0.05 weight percent
 [0050] MgO—0.05 weight percent;
 and preferably:
 [0051] Na₂O—0.01 weight percent
 [0052] SiO₂—0.01 weight percent
 [0053] Al₂O₃—0.01 weight percent
 [0054] TiO₂—0.01 weight percent
 [0055] Fe₂O₃—0.01 weight percent
 [0056] CaO—0.025 weight percent
 [0057] MgO—0.025 weight percent.

Other specific concentration ranges of stabilizers are provided in co-pending and commonly assigned U.S. patent applications entitled "CERAMIC MATERIAL FOR HIGH TEMPERATURE SERVICE," "OPTIMIZED HIGH TEMPERATURE THERMAL BARRIER," and "HIGH PURITY CERAMIC ABRADABLE COATINGS," each filed on Sep. 12, 2006 and each incorporated herein by reference.

[0058] FIG. 2 provides a phase diagram for pure zirconia. (The diagram can be found, for example, in Ceramic Phase Diagrams vol. 3, FIG. 04259.) As shown in FIG. 3, pure zirconia exists in three crystal phases at different temperatures. At very high temperatures (>2370° C.) the material has a cubic structure. At intermediate temperatures (1200 to 2372° C.) it has a tetragonal structure. At relatively lower temperatures (below 1200° C.) the material transforms to the monoclinic structure. The transformation from tetragonal to monoclinic is accompanied by a 3 to 5 percent volume increase that causes extensive stress in the material. Thus, pure zirconia cannot fulfill the coating requirements for high-temperature cycling. The resulting strain difference between the coating and substrate caused by the phase transformation results in a stress that is greater than the bond strength between them, so the coating will detach.

[0059] In order to overcome the volume change caused by the undesired phase transformation described above, one or more elements are added to the zirconia to modify the amount of phase transformation that occurs. The stabilizing elements, which are suitable for changing the amount and rate of phase transformation that occurs in the oxide coating, include the following: scandium, yttrium and the rare earths, particularly the lanthanides, since they have solubility in zirconia. Scandium is not typically used due to its rarity and resulting prohibitive cost. Rare earths metals from the actinide group such as uranium and thorium are not typically used due to their radioactivity. Thus, yttrium is a preferred stabilizing element. For purposes of the present invention, any of these elements used as stabilizing oxides (namely, any oxide from group IIIB (column 3) of the periodic table of elements) can be referred to as rare earth oxides.

[0060] FIG. 3 provides a standard phase diagram for stabilized zirconia showing the general alloying trends for the zirconia stabilizers. (The diagram can be found, for example, in Ceramic Phase Diagram, vol. Zirconia, FIG. Zr-157.) Zirconia can be either partially or fully stabilized. Fully stabilized zirconia has an crystal structure that is cubic at all temperatures up to melting. Partially stabilized zirconia has an crystal structure that is tetragonal and has a phase

transformation between tetragonal at higher temperatures and monoclinic plus cubic at lower temperatures. The temperature at which phase transformation occurs depends on the stabilizer material, as each stabilizer causes a different amount of suppression of the temperature of the onset of the tetragonal to monoclinic plus cubic phase transformation. At the suppressed temperatures, the rate of the phase transformation is greatly reduced. Over a large number of temperature cycles the phase transformation will slowly occur.

[0061] One possible theory is that the phase transformation in partially stabilized zirconia causes localized stresses that lead to the formation of micron-sized micro-cracks in the coating upon thermal cycling that cancel out some of the massive stress caused by coating volume shrinkage. Thus, these two phenomena of the coating structure—shrinking and cracking—work against each other and finding a balance between them will maximize coating lifetime. This mechanism implies then that the structure of the crack network of the coating is changing with time as the phase of the ceramic material changes. This mechanism is required for a thermal barrier or high temperature abradable coatings to survive thermal cycling.

[0062] From this theory, the composition for which the best possible balance between sintering and phase transformation exists. The most desired composition can be found empirically by making thermal cycling tests with samples of differing composition and measuring the number of thermal cycles to failure. FIG. 4 shows the results for yttria-stabilized zirconia. From FIG. 4 it can be seen that a composition around 6.5 weight percent has the longest lifetime when similar coatings of varying composition were tested.

[0063] The addition of a stabilizing element affects two main properties of the zirconia system in a positive manner. First, the addition of a stabilizer generally increases the melting temperature of the zirconia (in the partially stabilized composition ranges). Second, the addition of a stabilizer generally decreases the thermal conductivity. From the phase diagram in FIG. 5, which plots melting temperature versus composition, it can be seen that ytterbia stabilized zirconia (ZrYb₂O₅) and yttria stabilized zirconia (ZrY₂O₅) have the highest melting temperatures respectively for zirconia stabilizers (excluding actinides such as thoria that are radioactive and not fit for service). These stabilized compositions therefore have the greatest sintering resistance and, consequently, the greatest potential coating lifetime.

[0064] Rising fuel cost and other factors continue to drive the need for improved operational efficiency, and thus higher operating temperatures, of gas turbines. While yttria stabilized zirconia is the material of choice for stabilization, greater operational temperatures can be achieved using ytterbia, for example, as shown in FIG. 4. Zirconia partially stabilized by ytterbia provides a better composition, since it also has one of the lowest thermal conductivities of the potential stabilizers when alloyed with zirconia. As the need for higher operating temperatures increases, a higher coating material cost may be tolerated, so ytterbia partially stabilized zirconia may become a preferred thermal barrier. Given then the trade-offs of cost and performance, a combination of both yttria and ytterbia stabilizers is expected to have optimum performance to cost ratio

[0065] A thermal barrier coating can be further optimized by considering the effect of coating structure on lifetime.

Three types of structures exist depending on coating manufacturing method. Even though the general structures described herein have different complexities and are defined by differently sized spaces, they have one thing in common: they are physically made up of cracks, whose initial structure is defined by the manufacturing method of the material and coating and whose crack structure changes with time. These structures can be formed using the partially stabilized zirconia and/or hafnia material variants of the present invention, as described above with respect to FIGS. 2-5.

[0066] The ceramic coating in embodiments of the present invention has anisotropic sintering. For the coating made up of frozen splats with respect to FIGS. 6 and 7, high temperature shrinkage or sintering occurs less in the in-plane direction than in the through thickness direction. FIG. 6 provides a diagram showing a lamellar thermal barrier coating structure 120 containing porosity and micro cracks. The coating 120 is made up of frozen splats 111 applied over a substrate 100 and optional bond coat 112. FIG. 7 provides a diagram showing a lamellar thermal barrier coating structure 130 containing macro cracks, porosity and micro cracks. The coating 120 is made up of frozen splats 131 applied over a substrate 100 and optional bond coat 112. The coating 130 has vertical macro cracks 132 through the thickness of the coating. For a coating made up of frozen splats, as shown in FIGS. 6 and 7, this phenomenon can be explained by the structure that is formed. The coating has many more splat boundaries in the through thickness direction than in the in-plane direction, so it is the boundaries between splats sintering together that results in the shrinkage in the through-thickness. Thus, the sintering resistance of the coating can be improved by using yttria partially stabilized zirconia and/or hafnia and yttria stabilized zirconia and/or hafnia together. FIG. 11A shows a resulting coating 160 structure (applied over optional bond coat 112 and substrate 110), where the frozen droplets of yttria partially stabilized zirconia and/or hafnia 111 are interspersed with splats of yttria stabilized zirconia and/or hafnia 162. FIG. 11B shows a resulting coating 170 structure (applied over optional bond coat 112 and substrate 110) including vertical cracks 132, where the frozen droplets of yttria partially stabilized zirconia and/or hafnia 111 are interspersed with splats of yttria stabilized zirconia and/or hafnia 162. One method of achieving this structure is by blending particles of each of the aforementioned in order to create some percentage splat boundaries that contain yttria stabilized zirconia on either one or both sides. An additional benefit of this coating will be that it has a lower thermal conductivity than a coating made from yttria stabilized zirconia and/or hafnia alone.

[0067] As previously noted, zirconia is transparent to radiation in the infrared range. Thus the effectiveness of typical zirconia barrier systems will decrease more rapidly at temperatures around 1500° C., when radiation becomes the dominant method of heat transfer. There are two stabilizers for zirconia from the lanthanide series that, when added to zirconia, form an atomic oxide structure that serves to scatter photons in the infrared range. These stabilizers are europia (Eu₂O₃) and neodymia (Nd₂O₃). Both neodymia and europia are effective stabilizers, but neodymia may be the more preferable due to its lower cost. The europia and neodymia can also be combined. In order to further optimize the thermal barrier coating at high temperatures, europia or neodymia are specifically added to the zirconia-based pow-

der material, so that the thermal conductivity of the coating is optimized at high temperatures.

[0068] Thus, in embodiments of the invention the material includes zirconia (ZrO₂) and/or hafnia (HfO₂) wherein the zirconia and/or hafnia is partially stabilized by the neodymium (Nd₂O₃) and/or europia (Eu₂O₃) and the total amount of impurities is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of stabilizers is:

[0069] Nd₂O₃—4-20 weight percent

[0070] Eu₂O₃—4-16 weight percent

[0071] Nd₂O₃ and Eu₂O₃—4-16 weight percent

and preferably:

[0072] Nd₂O₃—8-16 weight percent

[0073] Eu₂O₃—10-16 weight percent

[0074] Nd₂O₃ and Eu₂O₃—4-16 weight percent

[0075] Oxide impurities include soda (Na₂O), silica (SiO₂), and alumina (Al₂O₃), as well as titania (TiO₂) hematite (Fe₂O₃), calcia (CaO), and magnesia (MgO). The limits for these known oxide impurities in order to achieve a desirable sintering rate and therefore increase service lifetime when used as a coating are the same as those listed above with respect to previous compositions.

[0076] A blend of two or more partially stabilized high-purity material compositions may also be used. For example, in another embodiment, a blended ceramic material for use in high-temperature thermal barriers is provided. The blended materials include a first material with a yttria (Y₂O₃) stabilizer, and a balance of at least one of zirconia (ZrO₂) and hafnia (HfO₂) and combinations thereof, wherein the zirconia (ZrO₂) and/or hafnia (HfO₂) is partially stabilized by the yttria stabilizer, and wherein the total amount of impurities of the first material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Y₂O₃ stabilizer is about 4-12 weight percent, and preferably 6-9 weight percent. The second material of the blended material may contain a ytterbia (Yb₂O₃) stabilizer and a balance of at least one of zirconia (ZrO₂) and hafnia (HfO₂) and combinations thereof, wherein the zirconia (ZrO₂) and/or hafnia (HfO₂) is partially stabilized by the ytterbia stabilizer, and wherein the total amount of impurities of the second material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Yb₂O₃ stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. In the blended material, the ytterbia (Yb₂O₃) stabilized zirconia (ZrO₂) and/or hafnia (HfO₂) fraction may include about 5-50 weight percent of the total and preferably about 15-30 weight percent of the total. The yttria stabilized zirconia (ZrO₂) and/or hafnia (HfO₂) fraction may include about 50-95 weight percent of the total and preferably about 70-85 weight percent of the total blend.

[0077] In another embodiment the blended material includes a first material with a ytterbia (Yb₂O₃) stabilizer, and a balance of at least one of zirconia (ZrO₂) and hafnia (HfO₂) and combinations thereof, wherein the zirconia (ZrO₂) and/or hafnia (HfO₂) is partially stabilized by the ytterbia stabilizer, and wherein the total amount of impurities of the first material is less than or equal to 0.15 weight

percent, and preferably less than or equal to 0.10 percent. The range of Yb_2O_5 stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. The second material of the blended material may contain a stabilizer of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof and a balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the balance is partially stabilized by the stabilizer, and wherein the total amount of impurities of the second material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Nd_2O_3 stabilizer is about 4-20 weight percent, and preferably 8-16 weight percent. The range of Eu_2O_3 stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. The range of the combined Nd_2O_3 and Eu_2O_3 stabilizer is about 4-16 weight percent. In the blended material, the yttria (Y_2O_3) stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 5-50 weight percent of the total and preferably about 15-30 weight percent of the total. The yttria stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 50-95 weight percent of the total and preferably about 70-85 weight percent of the total blend.

[0078] In another embodiment of the invention the blended material includes a first material with a yttria (Y_2O_3) stabilizer, and a balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the yttria stabilizer, and wherein the total amount of impurities of the first material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Y_2O_3 stabilizer is about 4-12 weight percent, and preferably 6-9 weight percent. The second material of the blended material may contain a stabilizer of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof and a balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the balance is partially stabilized by the stabilizer, and wherein the total amount of impurities of the second material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Nd_2O_3 stabilizer is about 4-20 weight percent, and preferably 8-16 weight percent. The range of Eu_2O_3 stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. The range of the combined Nd_2O_3 and Eu_2O_3 stabilizer is about 4-16 weight percent. In the blended material, the neodymium (Nd_2O_3) and/or europia (Eu_2O_3) stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 5-50 weight percent of the total and preferably about 15-30 weight percent of the total. The yttria stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 50-95 weight percent of the total and preferably about 70-85 weight percent of the total blend.

[0079] In a further embodiment of the invention the blended material includes a blend of at least three materials. The first material may contain a yttria (Y_2O_3) stabilizer, and a balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the yttria stabilizer, and wherein the total amount of impurities of the first material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Y_2O_3 stabilizer is about 4-12 weight percent, and preferably 6-9 weight percent. The second material of the blend may contain a yttria (Y_2O_3) stabilizer, and a

balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the yttria stabilizer, and wherein the total amount of impurities of the second material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Yb_2O_5 stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. The third material of the blend may contain a stabilizer of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof and a balance of at least one of zirconia (ZrO_2) and hafnia (HfO_2) and combinations thereof, wherein the balance is partially stabilized by the stabilizer, and wherein the total amount of impurities of the third material is less than or equal to 0.15 weight percent, and preferably less than or equal to 0.10 percent. The range of Nd_2O_3 stabilizer is about 4-20 weight percent, and preferably 8-16 weight percent. The range of Eu_2O_3 stabilizer is about 4-16 weight percent, and preferably 10-16 weight percent. The range of the combined Nd_2O_3 and Eu_2O_3 stabilizer is about 4-16 weight percent. In the blended material, the yttria (Y_2O_3) stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 5-45 weight percent of the total, and preferably about 15-30 weight percent of the total. The neodymium (Nd_2O_3) and/or europia (Eu_2O_3) stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may also include about 5-45 weight percent of the total and preferably about 15-30 weight percent of the total. The yttria stabilized zirconia (ZrO_2) and/or hafnia (HfO_2) fraction may include about 10-90 weight percent of the total, and preferably about 30-60 weight percent of the total blend.

[0080] The partially stabilized high-purity materials and blends described above may be supplied in the form of a powder, solution, suspension, ingot or target. Powder may be in the form of a spray dried powder of the individual constituents and organic binder, spray dried powder of the combined individual constituents and organic binder, fused and crushed powder, agglomerated and sintered powder, plasma densified material or powder from chemical solution routes. Typical particle sizes may vary but are typically between about 5-150 microns when deposited by various thermal spray equipment, preferably between about 15-125 microns for air plasma spray. Particle sizes are typically less than about 45 microns, preferably less than about 30 microns, for low pressure plasma spray.

[0081] FIG. 12 provides a diagram showing a thermal barrier coating structure 190 formed from a blend of components 111, 162 and a placeholder 192. The placeholder material 192, made of an organic powder material or an inorganic powder material, can be burned out subsequent to deposition. The organic or inorganic powder material has particle sizes typically between about 5-150 microns, and preferably between about 15-125 microns for plasma spray. The placeholder material 192 may be combined with the material blends described above to provide an material for an applied coating structure with porosity. In certain embodiments, the blended material is about 70-90 volume percent of the total material blended with 10-30 volume percent of the placeholder material, and preferably 15-30 volume percent.

[0082] Using the materials and the material blends described above, a high purity coating structure suitable for high temperature cycling applications may be formed by DC

or RF plasma or combustion spraying in air or inert atmospheres at pressures between 1 Pa and 1 MPa. Alternatively, the materials may be co-sprayed in the ratios of the materials described above. As shown in FIGS. 6 and 11A, when the material are applied in accordance with these procedures, the resultant coating may contain a lamellar collection of frozen droplets and semi-molten droplets applied to a metal substrate forming a ceramic matrix, porosity and micro cracks. FIG. 6 provides a diagram showing a lamellar thermal barrier coating structure formed from liquid droplets, and FIG. 11A provides a diagram showing a lamellar thermal barrier coating structure formed from a blend of components. The porosity of the lamellar thermal barrier coating structure refers to a void with an aspect ratio (length divided by width) of less than about 10. Typical porosity is in the range of about 2~20 volume %, and preferably in the range of 7~15 volume %. The micro cracks refers to a void with an aspect ratio (length divided by width) of larger than about 10 and the length of the void is less than about 100 micrometers. Typical volume percentage of micro cracks is in the range of about 2~10 volume %, and preferably in the range of about 2~7 volume %.

[0083] The material and material blends discussed above may also be applied as a lamellar collection of frozen droplets and semi-molten droplets applied to a heated metal substrate to form a ceramic matrix, porosity, macro cracks and micro cracks. These structures are shown in FIGS. 7 and 11B. The porosity refers to a void with an aspect ratio (length divided by width) of less than about 10. Typical porosity for this structure is less than about 12 volume %, and preferably less than about 5 volume %. The macro cracks refer to a void with an aspect ratio (length divided by width) of larger than about 10 and the length of the void is longer than about 100 micrometers. More than about 90% of the macro cracks are arranged in the direction normal to the top coat and substrate interface. These macro cracks are referred to as vertical macro cracks, while the macro cracks parallel to the top coat and substrate interface are referred to as horizontal macro cracks. The average number of vertical macro cracks in a length of 25.4 mm along the top coat and substrate interface is in the range of about 5 to 250, preferably in the range of about 50 to 150. The structure may be subsequently heat-treated and cooled to form additional macro cracks perpendicular to the coating and substrate interface.

[0084] Using a different application process, the material and material blends discussed above may also be applied to form a high purity coating structure having ceramic columns and gaps between the columns, as shown in FIG. 8. The materials may be applied using a vapor deposition process such as low pressure plasma spraying or physical vapor deposition in air or inert atmospheres at pressures between 1 mPa and 1 kPa. When coatings are produced using a vapor deposition process, the resulting coating has a unique columnar structure. The gaps between columns impart excellent strain tolerance to the coating. As illustrated in FIG. 8, if vapor deposition process was employed, another high purity coating structure 140 that comprises ceramic columns 143 and gaps 141 between them can be achieved. An optional bond coat 112 is shown between the substrate 100 and the coating 140. The high purity coating structure 140 is formed by vaporizing the inventive high purity materials in a form of powder, ingot, target, solution or suspension. The formed vapor then deposited atomically on

the substrate. By controlling processing temperature and pressure according to the Thornton's model (FIG. 9), a coating with columnar structure is formed. Herein, ceramic columns 143 are basically a cluster of crystals. In low pressure (lower than ambient) plasma spraying process, if molten droplets are also generated during the vaporization of the invention high purity materials, then the entrapment and incorporation of these droplets into the coating results in the formation of another high purity coating structure. The ceramic columns are basically a cluster of crystals. In this structure, more than about 90% of the crystals are oriented at an angle of about 45 to 135 degrees to the top coat and substrate interface. Within the cluster of crystals, voids smaller than about 20 micrometers may be present. The gaps between the columns have an aspect ratio (length divided by width) of larger than about 10. More than about 90% of the gaps are oriented at an angle of about 45 to 135 degrees to the top coat and substrate interface. The frozen droplets distributing randomly in the gaps and columns are typically less than about 45 micrometers, and preferably less than 30 micrometers.

[0085] The material and material blends discussed above may also be applied to form a structure with ceramic columns, gaps between the columns and frozen droplets distributing randomly in the gaps and columns. As illustrated in FIG. 10, the high purity coating structure 150 comprises ceramic columns 143, gaps between the columns 141, and nodules 142 distributing randomly in the gaps and columns. An optional bond coat 112 is shown between the substrate 100 and the coating 150. The nodules 142 distributing randomly in the gaps and columns are frozen droplets. The size of these nodules 142 is typically less than about 45 micrometers, preferably less than about 30 micrometers. FIG. 11C provides a diagram showing a columnar thermal barrier coating structure 180 formed from a blend of components. The coating structure of FIG. 11C includes the same components as shown in FIG. 10 and further includes a second coating material 182 interspersed throughout the ceramic columns 143. The ceramic columns are basically a cluster of crystals. In this structure, more than about 90% of the crystals are oriented at an angle of about 45 to 135 degrees to the top coat and substrate interface. Within the cluster of crystals, voids smaller than about 20 micrometers may be present. The gaps 141 between the columns have an aspect ratio (length divided by width) of larger than about 10. More than about 90% of the gaps are oriented at an angle of about 45 to 135 degrees to the top coat 180 and substrate 100 interface.

[0086] In accordance with the invention, a thermal barrier or high temperature abradable seal coating can be further optimized by building the coating in layers with different compositions, or by introducing a compositional gradient through the thickness of the coating. The reason for this is that due to the relatively low thermal conductivity of the coating, a temperature gradient exists in the coating during high temperature surface, since the substrate is being cooled. Thus there is a variation in the sintering rate through the thickness of the coating, and this means that the coating structure can be designed using the most optimal material at the surface, with less optimal materials towards the interface. Compositional gradients can be introduced into the coating during manufacture by using multiple feedstocks of different composition and varying their feed-rates during deposition. A coating with a compositional gradient is

shown in FIG. 13, where the coating includes a starting material 261 most prominent along the surface of substrate 100 (or optional bond coat 112) and gradually giving way to starting material 262, which makes up most of the exterior surface of the coating 260. Materials 261 and 262 may be any of the materials described above with respect to embodiments of the present invention. Coating structures for the compositional gradients may include any of the structures described above.

[0087] In addition to optimizing the coating by using compositional gradients, the coating can also be optimized by manufacturing it in layers with different compositions. The coating can have two or more layers, or multiple repeating layers. For example of one embodiment, as shown in FIG. 14, a coating 270 with a top layer 271 made from a material with optimized sintering resistance (for example, yttria stabilized zirconia according to embodiments of the present invention), a middle layer 272 with photon scattering capabilities (for example, neodymia and/or europia stabilized zirconia according to embodiments of the present invention) and a bottom layer 273 made from a third composition (for example, zirconia stabilized with yttria or scandia or a lanthanide oxide according to embodiments of the present invention). Another example is FIG. 15, showing a coating 280 with a repeating pattern of layers including a top layer 271, middle layer 272, and bottom layer 273 repeated, as shown. The combinations in FIGS. 14 and 15 serve only as examples. One skilled in the art will recognize numerous material combinations and coating structures as described herein may be layered to achieve optimal coating performance for various service conditions.

[0088] While exemplary embodiments of the invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous insubstantial variations, changes, and substitutions will now be apparent to those skilled in the art without departing from the scope of the invention disclosed herein by the Applicants. Accordingly, it is intended that the invention be limited only by the spirit and scope of the claims, as they will be allowed.

We claim:

1. A blended high-purity coating that is suitable for high temperature cycling applications, said coating comprising:

a first material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer; and

a second material of a different composition than the first material, said second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer;

wherein the first and second materials are blended together in the coating, and wherein the total amount of impurities in the coating is less than or equal to 0.15 weight percent.

2. The blended high-purity coating of claim 1, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 16 weight percent ytterbia.

3. The blended high-purity coating of claim 1, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

4. The blended high-purity coating of claim 1, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 16 weight percent ytterbia (Yb_2O_3), and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

5. The blended high-purity coating of claim 1, further comprising a third material of a different composition than the first and second materials, said third material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer.

6. The blended high-purity coating of claim 1, further comprising a placeholder material made of an organic powder material or an inorganic powder material that can be burned out subsequent to deposition of the blended material, said placeholder material comprising about 10-30 volume percent of the total materials.

7. The blended high-purity coating of claim 1, wherein the total amount of impurities in the coating is less than or equal to 0.10 weight percent.

8. The blended high-purity coating of claim 1, wherein the coating has a structure including a ceramic matrix, porosity, and micro cracks.

9. The blended high-purity coating of claim 1, wherein the coating has a structure including a ceramic matrix, porosity, macro cracks, and micro cracks.

10. The blended high-purity coating of claim 1, wherein the coating has a structure including ceramic columns and gaps between the columns.

11. A high-purity coating structure that is suitable for high temperature cycling applications, said coating structure formed by the process comprising the steps of:

providing a first material in a form suitable for use in thermal spraying applications, wherein said first material consists essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in the first material is less than or equal to 0.15 weight percent;

providing a second material of a different composition than the first material and in a form suitable for use in

thermal spraying applications, said second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in second material is less than or equal to 0.15 weight percent; and

applying each of said materials onto a metal substrate so that the materials are blended in the coating.

12. The high-purity coating structure of claim 11, wherein the applying step is accomplished using a thermal spray process conducted at pressures between 1 Pa and 1 MPa, so as to form a stream of molten and/or semi-molten droplets that build up a coating of frozen lamellar splats subsequent to impact with the substrate.

13. The high-purity coating structure of claim 12, wherein the coating has a structure including a ceramic matrix, porosity, and micro cracks.

14. The high-purity coating structure of claim 12, wherein the coating has a structure including a ceramic matrix, porosity, macro cracks, and micro cracks.

15. The high-purity coating structure of claim 11, wherein the applying step is accomplished using a vapor deposition process conducted at pressures between 1 mPa and 1 kPa, so as to form a coating with ceramic columns and gaps between the columns.

16. The high-purity coating structure of claim 11, wherein the applying step is accomplished using a low pressure plasma spray process conducted at pressures between 1 Pa and 10 kPa, so as to form ceramic columns, gaps between the columns, and frozen droplets distributed randomly in the gaps and columns.

17. The high-purity coating structure of claim 11, wherein the formation process further comprises the step of providing a placeholder material made of an inorganic powder material or an organic powder material that can be burned out subsequent to deposition of the blended material, said placeholder material comprising about 10-30 volume percent of the total materials.

18. The high-purity coating structure of claim 11, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 16 weight percent ytterbia.

19. The high-purity coating structure of claim 11, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

20. The high-purity coating structure of claim 11, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 16 weight percent ytterbia (Yb_2O_3), and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

21. The high-purity coating structure of claim 11, further comprising a third material of a different composition than the first and second materials, said third material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer.

22. A method for producing a high-purity coating structure suitable for high temperature cycling applications, said method comprising the steps of:

providing a first material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities is less than or equal to 0.15 weight percent;

providing a second material of a different composition than the first material, said second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer, and wherein the total amount of impurities in second material is less than or equal to 0.15 weight percent; and

applying said materials onto a metal substrate.

23. The method of claim 22, wherein the first and second materials are supplied in the form of a powder or a slurry of partially stabilized powder, and wherein said step of applying uses a thermal spray process.

24. The method of claim 23, wherein said thermal spray process is conducted at pressures between about 1 Pa and 1 MPa, so as to form a stream of molten and/or semi-molten droplets that build up a coating of frozen lamellar splats subsequent to impact with the substrate.

25. The method of claim 24, wherein the thermal spray process results in a coating having a structure including a ceramic matrix, porosity, and micro cracks.

26. The method of claim 24, wherein the thermal spray process results in a coating having a structure including a ceramic matrix, porosity, macro cracks, and micro cracks.

27. The method of claim 22, wherein the first and second materials are applied using a vapor deposition process.

28. The method of claim 27, wherein said vapor deposition process is conducted at pressures between 1 mPa and 1 kPa, so as to form a coating with ceramic columns and gaps between the columns.

29. The method of claim 27, wherein said vapor deposition process is a low pressure plasma spray process conducted at pressures between 1 Pa and 10 kPa, so as to form ceramic columns, gaps between the columns, and frozen droplets distributed randomly in the gaps and columns.

30. The method of claim 22, wherein further comprising providing a placeholder material made of an inorganic powder material or an organic powder material that is burned out subsequent to deposition of the blended material, said placeholder material comprising about 10-30 volume percent of the total materials.

31. The method of claim 22, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 16 weight percent ytterbia.

32. The method of claim 22, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 12 weight percent yttria, and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

33. The method of claim 22, wherein said first material is about 5 to 50 weight percent of the total coating and the stabilizer of said first material is about 4 to 16 weight percent ytterbia (Yb_2O_5), and wherein said second material is about 50 to 95 weight percent of the total coating and the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof.

34. The method of claim 22, further comprising providing a third material of a different composition than the first and second materials, said third material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer.

35. The method of claim 22 wherein said step of applying comprises co-spraying said first material and said second material.

36. A graded high-purity coating that is suitable for high temperature cycling applications, said coating comprising:

a first material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer; and

one or more second material of a different composition than the first material, said one or more second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer;

wherein the first and one or more second materials form a compositional gradient through the thickness of the coating, and wherein the total amount of impurities in the coating is less than or equal to 0.15 weight percent.

37. A layered high-purity coating that is suitable for high temperature cycling applications, said coating comprising:

a first material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer; and

one or more second material of a different composition than the first material, said one or more second material consisting essentially of about 4 to 20 weight percent of a stabilizer of one or more rare earth oxides, and a balance of at least one of zirconia (ZrO_2), hafnia (HfO_2) and combinations thereof, wherein the zirconia (ZrO_2) and/or hafnia (HfO_2) is partially stabilized by the stabilizer;

wherein the first and one or more second materials are layered through the thickness of the coating, and wherein the total amount of impurities in each coating layer less than or equal to 0.15 weight percent.

38. The method of claim 37, wherein the stabilizer of said first material is about 4 to 12 weight percent yttria; wherein the stabilizer of said second material is about 4 to 20 weight percent of at least one of neodymium (Nd_2O_3), europia (Eu_2O_3), and combinations thereof; and wherein the stabilizer of a third material is about 4 to 16 weight percent ytterbia.

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