

MODIFIED THERMAL BARRIER COMPOSITE COATINGS

Field of the Invention

[0001] The present invention relates generally to the field of thermal barrier composite coatings utilized to protect substrate materials from high temperature and corrosive environments.

Background of the Invention

[0002] Thermal barrier coatings (hereinafter, referred to as "TBC's") applied onto a substrate are known to inhibit the flow of heat into the substrate. TBC's are commonly utilized to protect alloy components of gas turbine engines that are exposed to hot combustion gases.

[0003] TBC's can be deposited by vapor processes, such as physical vapor deposition (PVD). Such PVD coatings typically are produced from process conditions designed to foster nucleation and growth of discrete, tightly packed, columnar grains which provides a compliant microstructure. The columnar grains are separated by small gaps that can relieve the stress in the coating. However, the gaps between the columns can provide pathways for penetration of contaminants which can induce corrosion of the underlying coating and/or substrate material.

[0004] As an alternative, thermal barrier coatings can be applied by atmospheric plasma spray (APS) which are derived from a dry powder source. APS coatings are formed by heating a gas-propelled spray of a powdered metal oxide or non-oxide material with a plasma spray torch. The spray is heated to a temperature at which the powder particles become molten. The spray of molten particle is directed against a substrate surface where they solidify upon impact to create a coating. The conventional as-deposited APS microstructure is known to be characterized by overlapping splats of material. The inter-splat boundaries can be tightly joined or may be separated by gaps resulting in some porosity. APS coatings are generally less expensive to apply than EB-PVD coatings and they provide a better thermal and chemical seal against the surrounding environment than columnar-grained structures. However, the inter-splat gaps in the as-

deposited APS microstructure tend to densify upon exposure to high temperatures. Such densification may result in a shorter operating life in a gas turbine environment by virtue of repeated thermal cycling inducing accumulation of thermal stresses within the coating that can ultimately cause spallation.

[0005] A columnar structure may be produced by using an APS process (i.e., spray process performed under ambient temperature and pressure conditions) utilizing nano-sized powder commonly delivered by solution or suspension means. The inter-columnar gaps can provide strain relief. When the plasma effluent and the particle size are tailored to a desired interaction range, the overlapping layers of deposited material can flow together to form a columnar ordering of the adjacent particle layers. While such a columnar structure may have some advantages when compared to the conventional as-deposited APS microstructure, these coatings have drawbacks, including low erosion resistance when tailored to have low intra-columnar densities; a direct heat path along the inter-columnar gaps; and/or potentially low resistance to chemical infiltration due to inter-columnar gaps and low intra-columnar densities.

[0006] In view of the drawbacks of conventional TBC's, there is an unmet need for TBC's with a compliant structure that can maintain adhesion to the substrate during thermal cycling while protecting the integrity of the substrate by inhibiting heat flow towards the substrate surface and blocking pathways for penetration of contaminants which can induce corrosion and/or erosion of the substrate surface.

Summary of the Invention

[0007] The invention may include any of the following aspects in various combinations and may also include any other aspect of the present invention described below in the written description.

[0008] The present invention offers a coating system that allows for a single coating structure to exhibit properties previously considered mutually exclusive. The present invention also offers a unique approach for tailoring specific properties of a coating structure as a function of location within the coating.

[0009] In a first aspect, a thermal barrier modified composite coating is provided, comprising: a first coating layer bonded to a surface of a substrate, said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer; said macro columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermo-mechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating; said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; and wherein said second coating layer is bonded to the corresponding free surfaces of the first coating layer, said second coating layer at the bulk and/or free surface having at least one improved coating property in comparison to the first coating layer.

[00010] In a second aspect, a thermal barrier modified composite coating is provided, comprising: a first coating layer bonded to a surface of a smooth substrate, said first coating layer having a size less than about 10 μm ; said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer; said macro columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermomechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating; said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; and said second layer comprising a densified coating layer bonded to the corresponding free surfaces of the first coating layer, said densified coating having a lower porosity than that of the first coating layer, said densified

coating having an improved mechanical erosion barrier in comparison to the first coating layer.

[00011] In a third aspect, a thermal barrier modified composite coating, is provided comprising: a first coating layer bonded to a surface of a smooth substrate, said first coating layer having a size less than about 10 μm ; said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer; said macro columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermomechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating; said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; said second layer comprising a densified coating layer bonded to the corresponding free surfaces of the first coating layer, said densified coating having a lower porosity than that of the first coating layer, said densified coating derived from a dry powder applied by atmospheric spraying, said coating comprising partially molten and fully molten particles having an improved mechanical erosion barrier in comparison to the first coating layer.

Brief Description of the Drawings

[00012] The above and other aspects, features, and advantages of the present invention will be more apparent from the following, more detailed description thereof, presented in conjunction with the following drawings, wherein:

[00013] Figure 1a shows an optical micrograph of a representative first coating layer of the present invention having columnar grained macrostructures;

[00014] Figure 1b shows an optical micrograph of the columnar grained coating of Fig. 1a at a higher magnification;

[00015] Figure 2 generally illustrates any suitable second coating layer that can be bonded to the free surfaces of the first coating layer of Figures 1a and 1b;

[00016] Figure 3 illustrates an exemplary composite coating system in

accordance with an embodiment of the present invention in which the second coating layer is a dense columnar coating;

[00017] Figure 4 illustrates an exemplary composite coating system in accordance with another embodiment of the present invention, in which the second coating layer is a environmental barrier coating;

[00018] Figure 5 illustrates an exemplary composite coating system in accordance with yet another embodiment of the present invention, in which the second coating layer is a DVC;

[00019] Figure 6 illustrates an exemplary composite coating system in accordance with yet another embodiment of the present invention, in which the second coating layer is an abradable coating;

[00020] Figure 7 shows an optical micrograph of a columnar composite coating system that was prepared in accordance with the principles of the present invention;

[00021] Figure 8 shows an optical micrograph for another columnar composite coating system that was prepared in accordance with the principles of the present invention;

[00022] Figure 9 plots and compares the results of various furnace cycle tests for different thermal barrier coating materials; and

[00023] Figure 10 plots and compares the results of various mechanical erosion resistance tests for different thermal barrier coating materials.

Detailed Description of the Invention

[00024] The objectives and advantages of the invention will be better understood from the following detailed description of the preferred embodiments thereof in connection. The present disclosure relates to novel TBC composite coatings for a variety of applications. The coatings of the present invention are particularly suitable for high-temperature applications, including, but not limited to gas turbines. The disclosure is set out herein in various embodiments and with reference to various aspects and features of the invention.

[00025] The relationship and functioning of the various elements of this invention are better understood by the following detailed description. The

detailed description contemplates the features, aspects and embodiments in various permutations and combinations, as being within the scope of the disclosure. The disclosure may therefore be specified as comprising, consisting or consisting essentially of, any of such combinations and permutations of these specific features, aspects, and embodiments, or a selected one or ones thereof.

[00026] A novel TBC composite coating system has been discovered with significantly improved performance characteristics. As will be discussed herein, the TBC's of the present invention can achieve improved performance, in relation to other types of materials, including conventional thermal barrier materials. Unless indicated otherwise, it should be understood that all compositions are expressed as weight percentages (wt %) based on the total weight of the formulation.

[00027] The TBC's of the present invention offer unique alternatives to conventional TBC's. In particular, the TBC's of the present invention include a first and a second layer which are selected to be compatible with each other so as to interact with each another in a synergistic manner to create and maintain superior thermomechanical compliance in terms of adhesion and bond strength at the coating-substrate interface while simultaneously improving selected coating properties in the bulk and/or free surface of the composite coating structure. The term "thermomechanical compliance" as used herein and throughout the specification is intended to refer to the ability of the first coating layer to maintain sufficient adhesion and bond strength to the substrate surface during repetitive thermal heating and cooling (i.e., "thermal cycling") so as to not undergo spallation from thermal shock impact that can be created by thermal cycling that occurs during use of the coated substrates in high temperature environments, such as, for example, gas turbine applications. In this manner, the composite coating structure is tailored to have one or more selected properties that may vary continuously within each of the first and/or second layers or in a discrete manner from a location within the first coating layer to a location within the second coating layer. The selected bulk properties may include, for example, bond

strength, thermal conductivity, erosion resistance, corrosion resistance, and thermomechanical compliance.

[00028] Exemplary first coating layers are shown in Figures 1a and 1b. Figure 1a shows an optical micrograph of a representative first coating layer 100 of the present invention having macro columnar features, and Figure 1b is an optical micrograph that shows the first coating layer 100 at higher magnification. Figures 1a and 1b show the first coating layer 100 bonded to a substrate 110. The first coating layer 100 serves as an undercoat for a second coating layer to be deposited thereon in the formation of a composite coating system. It should be understood that the terms “first coating layer” and “undercoat layer” will be used interchangeably throughout the specification. Figures 1a and 1b show the first coating layer 100 has macro columnar features 120. The macro columnar features 120 are comprised of microstructural features that include nano and/or sub-micron sized splats derived from a precursor liquid suspension of nano-sized and/or submicron sized precursor particles. It should be understood that the term liquid suspension as used herein is intended to refer to a suspension plasma spray (SPS) whereby fine particles as described herein can be effectively suspended and transported to the target substrate without substantial agglomeration to produce a coating. The majority of the precursor material are preferably splats which are partially molten and/or fully molten prior to impinging on the substrate 110. Any resultant particles that re-solidify prior to impacting the substrate 110 tend to become entrapped and lodged within the surrounding splats. The splats are randomly oriented to produce an isotropic crystallographic orientation in the first coating or undercoat layer 100. The portion of the splats bonded to the surface of the substrate 110 forms a thermomechanical compliant interface that can remain adhered to the surface during thermal cycling conditions typically encountered by TBC's.

[00029] Figures 1a and 1b further show that a controlled amount of porosity is built-in between adjacently configured macro columnar features 120 as well as within the macro columnar features 120. The built-in porosity of the columnar undercoat layer 100 can further improve thermomechanical compliance during

thermal cycling. As a result, the undercoat layer 100 can aid in extending the lifetime of the inventive TBC in comparison to conventional TBC's.

[00030] Figures 1a and 1b show that the macro-columnar features 120 of the undercoat layer 100 have a distinctive and unique feature of peaks 130 and valleys 140 along the free surfaces of the first coating layer. The term "free surfaces" as used herein in connection with the undercoat layer 100 is intended to refer to that portion of the first coating layer 100 that can bond with a topcoat or second coating layer, as will be discussed. It should be understood that the terms "topcoat layer" and "second coating layer" will be used interchangeably throughout the specification. The peaks 130 and valleys 140 can be better seen in the higher magnification of Figure 1b. Without being bound by any theory, it is believed that the peaks 130 and valleys 140 enhance the properties of the undercoat layer 100 in a manner that creates improved bonding and thermomechanical compliance between the undercoat layer 100 and a subsequent topcoat or second coating layer. The peaks 130 and valleys 140 can be produced to have a selected distribution and pattern based on control of the thermal spray process and coating media conditions. In a preferred embodiment, the peaks 130 and valleys 140 produce a random-like distribution to create an irregular free surface which is jagged and tortuous, as can be seen in Figure 1b. The degree of tortuosity of the undercoat layer 100 that is required may depend on several factors, including the end-use application and the type of second coating layer to be bonded thereto. Generally speaking, the tortuosity is sufficient to create a favorable interfacial boundary over which a second coating can be applied and remain adhered thereto during operational use of the composite coating. Figures 1a and 1b shows that the width and height of each of the peaks 130 and valleys 140 are substantially non-uniform in order to enhance the tortuosity along the free surface of the first coating layer 100.

[00031] The microstructure of the undercoat is defined by splats and grains contained within the splats. The grains are substantially non-equiaxed. The grains are produced by undergoing cooling and directional solidification upon making contact with the substrate 110 to produce an anisotropic crystallographic

orientation. The solidified grains within the splats acquire a directional orientation whereby the grains generally are aligned and grow in a preferred directionality, thereby creating localized texture.

[00032] The fine microstructural features of the undercoat layer 100 may be less than 25 microns (μm), and more preferably less than about 10 microns (μm) in size to enhance adhesion onto the substrate 110, which can be smooth. In another embodiment, the microstructural features of the undercoat range from about 10 μm down to about 50 nm in size or less. A smooth substrate as used herein is intended to mean a surface having a roughness (designated as "Ra") of less than about 125 μin . In one embodiment, the undercoat layer 100 of the present invention may be applied onto a smooth substrate surface characterized by a Ra between about 25 to about 80 μin . Surface preparation of the substrate surface is therefore not required prior to thermal spraying of the first coating layer 100 onto the substrate 110. This is in contrast to conventional thermal barrier coatings, which generally cannot adhere to a smooth surface without surface roughening of the substrate surface. Surface roughening is particularly detrimental to metal substrates such as gas turbine blades which are exposed to high temperature environments under which the metal surface of the substrate can oxidize and form an oxide layer which has a tendency to spall. The spallation is enhanced as a result of the accumulation of residual thermal stresses within the roughened oxide layer.

[00033] The first coating layer 100 therefore not only bonds to a smooth substrate surface, but can maintain thermomechanical compliance to the substrate 110 during the severe thermal cycling occurring during its lifetime, thereby extending the lifetime of the coated part such as a gas turbine assembly without requiring repair and/or restoration work.

[00034] Because the undercoat layer 100 is designed with a controlled amount of built-in porosity to improve thermomechanical compliance during thermal cycling, an extended lifetime of the TBC composite of the present invention in comparison to conventional TBC's can be achieved. The built-in porosity in combination with the tortuous interfacial boundary along the free

surfaces of the undercoat layer 100 can also enhance insulative properties of the composite coating.

[00035] The undercoat layer 100 by virtue of its relatively small size (i.e., sub-micron or smaller) can be prepared by suspending the precursor material in a liquid carrier during a thermal spray process utilizing a plasma torch to enable effective deposition and coverage of the sub-micron or smaller particles onto the substrate without particle agglomeration as would typically occur if the sub-micron particles were utilized as a dry powder. Suitable liquid carriers may include solvents which are aqueous based or fuels. In particular, suitable solvent materials include, by way of example and not intending to be limiting, water, ethanol, methanol, ethylene glycol, kerosene and propylene. The exact plasma torch conditions to be selected will be dependent upon several parameters, including the specific type of torch employed and the specific coating media selected for the undercoat and topcoat, as would be recognized by one of ordinary skill in the art.

[00036] Various thermal barrier precursor materials can be utilized for making the first coating layer 100, such as any suitable ceramic or cermet coating material. In one embodiment, a ceramic material such as a stabilized zirconia material may be used. Other examples include yttria-stabilized zirconia. Still further, oxides, such as hafnates and cerates can be used along with other oxides that may be stabilized with yttria or other stabilizing agents, such as, for example, ceria. The present invention also contemplates zirconium oxide, yttrium oxide, aluminum oxide or any other type of suitable rare earth oxide.

[00037] Although the columnar grained structure is thermomechanically compliant, it generally cannot on its own create the desired properties of a TBC. For these reasons, in accordance with the principles of the present invention as shown in Figure 2, it has been discovered that selection of a second coating layer or topcoat 200 that is compatible with the undercoat layer 100 of Figures 1a and 1b can be bonded thereto to produce a novel TBC composite coating system 220 in accordance with the principles of the present invention. For purposes of simplicity and conveying the versatility of the inventive aspect of the composite coating structure of the present invention, the topcoat 200 of Figure 2 is shown

not as a micrograph, but rather as an illustration whereby any suitable topcoat 200 can be selected that is complementary and compatible for bonding with the undercoat 100. For example, as Figure 2 illustrates, the top coat 200 may be selected as a dense TBC, an abradable coating or any other TBC as will be shown in greater detail in Figures 3-6. The tortuous free ends or free surfaces of the undercoat layer 100 provide an effective interfacial boundary 210 for the second coating layer 200 to bond thereto. In this manner, the one or more deficient properties of the first coating layer 100 can be offset or compensated by selection of a suitable second coating layer 200 that is not deficient in the same, thereby improving the overall performance of the TBC composite coating system 200 with respect to that particular deficient property. For instance, the first coating layer 100 by itself may contain an unacceptably high level of porosity which enhances thermomechanical compliance at the expense of not being able to effectively inhibit heat flow to the surface of the substrate 110. The second coating layer 200 can be selected that possesses sufficiently low thermal conductivity relative to the first coating layer 100 so as to balance or offset this particular deficiency in the first coating layer 100. Because the second coating layer 200 may be exposed to the high temperature environment of a component such as a combustion engine, its lower thermal conductivity inhibits heat flow much more effectively than the first coating layer 100. Additionally, the superior compliance of the first coating layer 100 maintains sustained integrity of the composite coating structure 220 in a manner that direct bonding of the second coating layer 200 to the substrate 110 cannot achieve. In other words, the direct bonding of the second coating layer 200 to the smooth or even roughened substrate surface 110 would potentially cause spallation and shorten the operational lifetime of the coated part.

[00038] As such, careful selection of compatible and complementary first and second coating layers 100 and 200 respectively, in accordance with the principles of the present invention creates a modified composite TBC composite structure 200 with properties not entirely present in the first coating layer or the second

coating layer but when in combination can synergistically improve the overall performance of the TBC in comparison to conventional TBC materials.

[00039] In accordance with principles of the present invention, various types of second coating layers can be applied onto the tortuous interface of the first coating layer. Of particular significance, selection of the appropriate second coating layer improves the overall bulk and free surface properties of the composite coating system without sacrificing loss of thermocompliance, as will be shown in the Examples. Possible composite coatings contemplated by the present invention are shown in Figures 3-6. It should be understood that Figures 3-6 are intended to be illustrative of certain aspects of the composite coating and in the process of doing so may not be representative of the macrostructural and/or microstructural coating morphology of the composite coating system.

[00040] Figure 3 shows a composite coating system 300 consisting of a densified columnar coating as the second coating layer 320 and a porous columnar coating 310 as the undercoat or first coating layer. The densified columnar coating 320 may be applied onto porous columnar undercoat 310 by any suitable process. In one embodiment, the densified columnar coating 320 is derived from a liquid suspension of particles having a median size greater than that of the median size of the first coating layer 310. The densified columnar coating 320 has a higher density and lower porosity than the undercoat layer 310. As a result, the densified columnar coating 320 provides erosion resistance at its free surface and/or bulk regions. The undercoat 310 is the first coating layer and has a columnar structure directly bonded to a smooth substrate 330. The columnar undercoat structure 310 is as described in Figs. 1a and 1b. The undercoat layer 310 has built-in porosity by virtue of its macro columnar structural features described and shown in Figures 1a and 1b. The porous undercoat 310 has greater porosity than the densified columnar coating 320 and therefore provides the requisite thermomechanical compliance to extend the lifetime of the composite coating system 300 in comparison to conventional composite TBC systems.

[00041] The composite coating system 300 of Figure 3 grades the density within the column from across the thickness of the coating. The density can be

graded in several ways. In one embodiment, the density increases along a path starting at a location within either the first coating layer 310, or adjacent to the interface of the first coating layer 310 and the second coating layer 320, and then extending in a direction towards a point on the free surface of the second coating layer 320. The grading can occur in a continuous manner or discrete manner. It should be understood that other coating properties may also be graded.

[00042] The densified columnar coating 320 preferably has a greater thickness than the first coating layer 310 to further enhance erosion resistance properties. This combination of superior thermomechanical compliance provided by the first coating layer 310 and improved coating properties in the bulk and/or free surface provided by the second coating layer 320 produces a compliant composite coating system 300 with superior erosion resistance not previously possible by conventional TBC composite systems.

[00043] Another embodiment of the present invention is shown in Figure 4. Figure 4 shows a composite coating system 400 consisting of an environmental barrier coating (EBC) topcoat 420 as the second coating layer and a porous columnar coating 410 as the undercoat or first coating layer that is bonded to a smooth substrate 430. The environmental barrier topcoat 420 blocks pathways for penetration of contaminants therein which can induce corrosion of the substrate surface 430. The corrosion resistance of the second coating layer 420 is higher than that of the first coating layer 410. The porous columnar coating 410 may be substantially identical to that of the first coating layer 310 of Figure 3. Alternatively, the undercoat 410 may be modified at its free surfaces as necessary to produce a customized predetermined distribution of peaks and valleys that can create the desired tortuosity at the interface to allow compatibility with the environmental barrier topcoat 420 so as to facilitate bonding and adhesion of the topcoat 420 thereto.

[00044] Yet another embodiment of the present invention is shown in Figure 5. Figure 5 shows a composite coating system 500 consisting of a densely vertically cracked (DVC) topcoat 520 as the second coating layer and a porous columnar coating 510 as the undercoat or first coating layer. The DVC topcoat

520 utilizes a dense vertically cracked microstructure to create a dense barrier for erosion resistance. The DVC topcoat 520 may in some instances serve as an EBC. The undercoat 510 is bonded to a smooth substrate 530 and maintains a level of thermomechanical compliance not attainable by the DVC topcoat 520 itself. Furthermore, the erosion resistance of the second coating layer 520 is higher than that of the first coating layer 510. The first coating layer 510 is relatively more porous and columnar and may be modified at its free surfaces in comparison to that of Figures 3 and 4 to allow compatibility with the DVC topcoat 520 at the bond interface. In this manner, a compliant composite coating system 500 is customized and created with superior erosion resistance not previously possible by conventional TBC composite systems.

[00045] Yet another embodiment of the present invention is shown in Figure 6. Figure 6 shows a composite coating system 600 consisting of an abradable topcoat 620 as the second coating layer and a porous columnar coating 610 as the undercoat or first coating layer which is bonded to a smooth substrate 630. The abradable topcoat 620 is selected to be compatible with the free surfaces of the undercoat 610 at the tortuous interface. During service, the abradable topcoat 620 provides a seal while the columnar undercoat 610 maintains the thermomechanical compliance and adhesion. In this manner, a compliant composite coating system 600 is created with superior sealant properties not previously possible by conventional TBC composite systems.

[00046] Applicants have performed several experiments to compare the thermomechanical compliance of the modified composite TBC's of the present invention with other materials by conducting furnace cycle tests (FCT's), as will now be discussed in the Examples below. In all of the FCT tests, a smooth Ni based superalloy substrate having a surface roughness Ra of about 25-40 μin was utilized. The substrate surface was not pre-roughened, but only lightly burnished to remove any impurities at the free surface prior to coating. A fine mesh media was utilized to attain a final surface roughness that was within a surface range of about 25-40 μin .

[00047] A commercially available Progressive Surface 100HE™ plasma torch was employed to prepare the SPS undercoats for the Baseline Coatings in Comparative Examples 1 and 2; the SPS undercoat and SPS top coat in Example 1; and the SPS undercoat in Example 2. Torch conditions when utilizing the Progressive Surface 100HE™ torch to prepare each of such coatings included gas flows and chemistries of 180 scfh argon; 120 scfh nitrogen; and 120 scfh hydrogen. The torch was operated at power levels of 100-105 kW and 450-500 Amps. The feedrate of the suspension feedstock was about 40-50 mL/min. The feedstock employed was an ethanol suspension of about 7-8wt% YSZ submicron sized particles. The suspension was radially injected into the plasma effluent externally of the Progressive Surface 100HE™. The torch was rastered across the part at a constant surface speed for a select number of passes until the desired coating thickness was accumulated.

[00048] The topcoat for the APS Densely Vertically Cracked (DVC) coating in Example 2 was produced using a PST 1100 series torch. The feedstock employed with the torch was an ethanol suspension of about 7-8wt% YSZ submicron sized particles. Plasma spray conditions were operated at 90 grams/minute of feedstock. The total current employed ranged from 150-170 Amps. The primary torch gas flows was 90 scfh torch gas; 90 scfh argon; and 40 scfh hydrogen gas.

[00049] Each FCT cycle consisted of exposing the coated sample to an elevated temperature of 2075F and holding at such temperature for 50 min followed by cooling the coated sample to 75F for 10 minutes. The average number of FCT cycles completed under such conditions was determined for each of the coatings tested. The coating was considered to fail after 20% of the total coating area was determined to spall from the substrate. A high number of FCT cycles prior to failure is desirable.

[00050] Coated samples were also prepared from the modified composite TBC's of the present invention and various other materials to test for resistance against mechanical erosion. Each mechanical erosion test was conducted under controlled conditions that consisted of subjecting the coated samples to angular-

shaped, alumina particles having a median size of 50 microns. The particles impinged the coated sample at a particle velocity of 200 ft/sec at 20C room temperature. An erosion rate is established for the test sample based on the exposure to a set mass of alumina erosion media. In other words, a mass of eroded coating material per mass of alumina erosion media is determined. A low erosion rate is desirable.

[00051] For all tested coated samples, the grain macrostructure was evaluated using optical microscopy.

Comparative Example 1 (Non-Composite Columnar SPS Structure)

[00052] A non-composite coating was prepared (designated Columnar SPS Baseline) from a feedstock material of 7-8wt% yttria stabilized zirconia (YSZ) in an ethanol-based suspension. The material had a submicron size of about 330 nm diameter. The material was suspended in the ethanol-based suspension and then thermally sprayed onto a smooth substrate having a surface roughness of about 25-40 μ in. A coating thickness of about 12 – 15 mil was obtained.

[00053] The resultant coating comprised macro columnar features. The column features were generally uniform in width across the surface of the substrate with each other. The features were also equivalent in height with each other. A regular smooth interface having uniform coating thickness was produced.

[00054] FCT cycles were performed to assess the thermomechanical performance of the non-composite coating. An average number of approximately 850 FCT cycles were completed, as shown by the bar labeled “Columnar SPS Baseline” in Figure 9.

[00055] Additionally coated non-composite samples were prepared for mechanical erosion testing. The erosion rate was determined in units of mg of tested material eroded per gram of alumina particle impinging the coated surface. This sample performed the worst of all tested materials, as evident by an erosion rate of approximately 1.05 mg/g, as shown by the bar labeled “Columnar SPS Baseline” in Figure 10.

[00056] These FCT and erosion test results were indicative of conventional TBC materials.

Comparative Example 2 (Non-Composite APS DVC)

[00057] A non-composite coating was prepared (designated APS DVC) from a feedstock material of 7-8 wt% YSZ dry powder. The material had a median particle diameter of 22 – 62 μm . The material was thermally sprayed by APS onto a smooth substrate having a surface roughness Ra of about 25-40 μin . It was observed that the APS DVC coating exhibited poor quality and coverage. The coating quality was too poor to produce any substantial coating, and only a maximum thickness of 1 mil was obtained in those regions where it was considered adherent.

[00058] FCT cycles were performed to assess the thermomechanical performance of the composite coating. The coating delaminated after only 20 total cycles, as shown by the bar in Figure 9 labeled “APS DVC”.

[00059] Additional coated non-composite samples were prepared for mechanical erosion testing. The erosion rate was determined in units of mg of tested material eroded per gram of alumina particle impinging the coated surface. The non-composite samples showed an erosion rate of between about .2-.25 mg/g, as shown by the bar labeled “APS DVC” in Figure 10.

[00060] These FCT and erosion test results were indicative of conventional TBC materials.

Example 1 (Composite Structure)

[00061] A composite coating system (designated “Columnar SPS Composite A”) was prepared as shown in Figure 7. The undercoat layer was prepared from feedstock of 7-8wt% yttria stabilized zirconia (YSZ). The undercoat material had a median particle diameter of about 330 nm. The undercoat material was suspended in an ethanol based suspension and then thermally sprayed onto a smooth substrate having a surface roughness Ra of about 25-40 μin . The coating thickness of the undercoat was 6 -7 mil.

[00062] The topcoat layer was prepared from a feedstock material of 7-8wt% YSZ. The top topcoat material had a median particle diameter of about 2 μm .

The topcoat material was suspended in a liquid carrier of an ethanol-based suspension and then thermally sprayed onto the substrate. The coating thickness of the topcoat was 4-5 mil. The thickness of the composite coating was 10 – 12 mil.

[00063] The resultant composite coating system produced is shown in Figure 7. The composite contained a porous macro columnar undercoat and a dense macro columnar top coat. The undercoat layer maintained thermomechanical compliance of the coating layer on the smooth substrate surface while the tortuous interfacial boundary provided improved mechanical bonding between the first and the second coating layers.

[00064] FCT cycles were performed to assess the thermomechanical performance of the composite coating. An average number of FCT cycles between 800-850 cycles were completed, as shown by the bar labeled “Columnar SPS Composite A” in Figure 9. The vertical lines extending from the top bars indicate standard deviation for the sample set for each of the tests. It was noted that the standard deviation showed that the Columnar SPS Composite A had an equivalent FCT performance to that of the Columnar SPS Baseline (Comparative Example 1) in which there was no statistical difference observed between the two coatings. It was therefore concluded that the Columnar SPS Composite A maintained equivalent FCT performance to the Columnar SPS Baseline (Comparative Example 1).

[00065] Additional coated composite samples were prepared for mechanical erosion testing. The erosion rate was determined in units of mg of tested material eroded per gram of alumina particle impinging the coated surface. The sample produced an erosion rate of about .3-.35 mg/g, as shown by the bar labeled “Columnar SPS Composite A” in Figure 10. The erosion results represented about a 70% improvement in erosion rate resistance in comparison to the coated sample of Comparative Example 1.

[00066] Contrary to the Comparative Example 1 baseline coating, the Columnar SPS Composite A coating maintained adequate FCT performance while also exhibiting the added benefit of superior erosion resistance.

Example 2 (Composite Structure)

[00067] A composite coating system (designated “Columnar SPS Composite B”) was prepared as shown in Figure 8. The undercoat layer was prepared from a feedstock of 7-8wt% yttria stabilized zirconia (YSZ). The undercoat material had a median particle diameter of about 330 nm. The undercoat material was suspended in an ethanol based suspension and then thermally sprayed onto a smooth substrate having a surface roughness Ra of about 25-40 μ in. The coating thickness of the undercoat was 6 -7 mils.

[00068] The topcoat layer was prepared from a feedstock material of 7-8 wt% YSZ dry powder having an average particle diameter between 22 – 62 μ m. The topcoat material was thermally sprayed by atmospheric plasma spraying (APS) onto a smooth substrate surface to produce an APS Densely Vertically Cracked (DVC) topcoat. The thickness of the APS DVC topcoat was about 8 mil and the total composite coating thickness was about 14-15 mil.

[00069] The resultant composite coating system is shown in Figure 8. The first coating or undercoat layer was more porous and provided thermomechanical compliance. The second coating or topcoat layer was denser and provided a barrier to mechanical erosion.

[00070] FCT cycles were performed to assess the thermomechanical performance of the composite coating. An average number of FCT cycles of about 800 cycles were completed, as shown by the bar labeled “Columnar SPS Composite B” in Figure 9. The vertical lines extending from the top bars indicate standard deviation for the sample set for each of the tests. It was noted that the standard deviation showed that the Columnar SPS Composite B had an equivalent FCT performance to that of the Columnar SPS Baseline (Comparative Example 1) in which there was no statistical difference observed between the two coatings. It was therefore concluded that the Columnar SPS Composite B maintained equivalent FCT performance to the Columnar SPS Baseline (Comparative Example 1).

[00071] Additional coated composite samples were prepared for mechanical erosion testing. The erosion rate was determined in units of mg of tested material

eroded per gram of alumina particle impinging the coated surface. The sample produced an erosion rate of slightly under .2 mg/g, as shown by the bar labeled "Columnar SPS Composite B" in Figure 10. The results represented about an 80% improvement in erosion rate resistance in comparison to the coated sample of Comparative Example 1.

[00072] Contrary to the Comparative Example 1 baseline coating, the Columnar SPS Composite B coating maintained adequate FCT performance while also exhibiting the added benefit of superior erosion resistance.

[00073] The Examples demonstrate that the inventive composite coatings of Examples 1 and 2 have the ability to maintain the thermomechanical compliance of a non-composite columnar coating (Comparative Example 1) while simultaneously achieving improved erosion resistance of an APS DVC (Comparative Example 2). Furthermore, the inventive composite coatings have the ability to bond and adhere to smooth substrate interfaces (e.g. < 100 μ in Ra), while also retaining thermal conductivity values consistent with thermal spray coatings. Additionally, the inventive TBC's are produced at a lower cost range in comparison to other typical thermal spray processes. Generally speaking, the ability for conventional TBC's to maintain thermomechanical compliance during repetitive thermal shock cycling was possible only at the expense of significantly reduced erosion resistance and other properties at the bulk and/or free surface of the coated sample. Examples 1 and 2 demonstrate that a specifically designed first coating layer having a non-uniform columnar macrostructure and bonded to a smooth substrate roughness enabled a subsequent second coating compatible with the first coating layer to be applied thereto.

[00074] The second coating is selected so as to complement the first coating layer by exhibiting one or more improved properties at the bulk and/or free surface of the resultant composite coating structure. In this manner, the present invention offers TBC composite structures that possess a combination of improved properties (e.g., thermomechanical compliance and erosion/corrosion resistance) previously recognized as mutually exclusive properties due to competing design considerations.

[00075] It should be understood that any suitable top coating can be utilized to provide desired bulk and free surface coating properties as may be desired for particular TBC applications as well as other types of applications. The specifically designed undercoat free surface may be modified as needed to ensure adequate bonding of the particular topcoat. For example, some topcoats may require increased tortuosity (i.e., increased non-uniformity in the heights and widths of adjacent peaks and valleys) of the free surfaces of the undercoat for adequate bonding of the topcoat.

[00076] Properties of the first coating layer are selectively tailored by virtue of the macrostructural features shown in Figures 1a and 1b. Of particular significance is the ability of the present invention to maintain adhesion to a smooth substrate and bond strength during thermal cycling, thereby producing materials with superior thermomechanical compliance in comparison to conventional thermal barrier coatings such as a DVC, abradable coating, environmental barrier coating or a densified columnar coating – none of which can typically maintain sustained adhesion and bond strength during thermal cycling.

[00077] While it has been shown and described what is considered to be certain embodiments of the invention, it will, of course, be understood that various modifications and changes in form or detail can readily be made without departing from the spirit and scope of the invention. It is, therefore, intended that this invention not be limited to the exact form and detail herein shown and described, nor to anything less than the whole of the invention herein disclosed and hereinafter claimed.

Claims

1. A thermal barrier modified composite coating, comprising:
 a first coating layer bonded to a surface of a substrate, said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer;

 said columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermomechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating;

 said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; and wherein said second coating layer is bonded to the corresponding free surfaces of the first coating layer, said second coating layer at the bulk and/or free surface having at least one improved coating property in comparison to the first coating layer.
2. The thermal barrier modified composite coating of claim 1, wherein said coating property is selected from the group consisting of thermal conductivity, erosion resistance, corrosion resistance and thermomechanical compliance.
3. The thermal barrier modified composite coating of claim 1, wherein said first coating layer further comprises built-in porosity in an amount greater than that of the second coating.
4. The thermal barrier modified composite coating of claim 1, wherein said second coating layer is selected from the group consisting of a dense vertically cracked coating, an abradable coating, an environmental barrier coating

a densified columnar coating, an atmospheric plasma sprayed coating and any combinations thereof

5. The thermal barrier modified composite coating of claim 1, wherein at least a portion of said peaks and valleys have a width and height substantially non-uniform to form an interfacial boundary with tortuosity.

6. The thermal barrier modified composite coating of claim 1, wherein said coating property is graded in a continuous manner within said second coating layer, wherein said coating property has a first value at first location adjacent to the interface of the first and the second coating layer, said property changing from said first value along a path starting at said first location and extending in a direction towards a point on the free surface of the second coating layer.

7. The thermal barrier modified composite coating of claim 1, wherein said coating property has a first value at a first location adjacent to the surface of the substrate and a second value at a point along a free surface of said second coating layer, wherein said coating property changes from said first value to said second value in a discrete manner.

8. The thermal barrier modified composite coating of claim 1, wherein said first coating layer comprises microstructural features of less than about 25 microns.

9. The thermal barrier modified composite coating of claim 1, wherein said first coating layer comprises microstructural features ranging from about 10 microns to about 50 nm.

10. A thermal barrier modified composite coating, comprising:

a first coating layer bonded to a surface of a smooth substrate, said first coating layer having a size less than about 10 μm ;

said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer;

said columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermomechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating;

said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; and

said second layer comprising a densified coating layer bonded to the corresponding free surfaces of the first coating layer, said densified coating having a lower porosity than that of the first coating layer, said densified coating having an improved mechanical erosion barrier in comparison to the first coating layer.

11. The thermal barrier modified composite coating of claim 10, wherein said microstructural features of said first coating layer have a size less than about 10 μm and equal to or greater than about 50 nm.

12. The thermal barrier modified composite coating of claim 10, wherein said densified coating is derived from a second precursor liquid suspension of nano-sized and/or submicron-sized particles.

13. The thermal barrier modified composite coating of claim 10, wherein said predetermined distribution of peaks and valleys are arranged to form an irregular interface having tortuosity.

14. The thermal barrier modified composite coating of claim 1, said first coating layer has built-in porosity in an amount greater than that of the densified coating.

15. A thermal barrier modified composite coating, comprising:
a first coating layer bonded to a surface of a smooth substrate, said first coating layer having a size less than about 10 μm ;

said first coating layer comprising macro columnar features characterized by a predetermined distribution of peaks and valleys at their corresponding free surfaces to create improved mechanical bonding between the first layer and a second layer;

said columnar features derived from a precursor liquid suspension of nano-sized and/or submicron-sized splats to form a thermomechanical compliant interface at the substrate surface, said splats being randomly oriented to produce an isotropic crystallographic orientation for the first coating;

said splats comprising non-equiaxed columnar grains that grow opposite to a direction of heat flow upon cooling to produce an anisotropic crystallographic grain orientation; and

said second layer comprising a densified coating layer bonded to the corresponding free surfaces of the first coating layer, said densified coating having a lower porosity than that of the first coating layer, said densified coating derived from a dry powder applied by atmospheric spraying, said coating comprising partially molten and fully molten particles having an improved mechanical erosion barrier in comparison to the first coating layer.

16. The thermal barrier modified composite coating of claim 15, wherein said particles of the densified coating layer have a size greater than about 10 μm .

17. The thermal barrier modified composite coating of claim 15, wherein said smooth substrate has a Ra of less than about 125 μin .

18. The thermal barrier modified composite coating of claim 17, wherein said smooth substrate has a Ra of less than about 80 μin .
19. The thermal barrier modified composite coating of claim 15, wherein said densified coating layer comprises at least one improved coating property in comparison to the first coating layer and further wherein said improved coating property is graded.
20. The thermal barrier modified composite coating of claim 15, wherein said densified coating layer produces a densely vertically cracked microstructure.