Technology: Thermal Barrier Coatings (TBCs)

Assignee: General Electric Company

USPTO search query [default ADJ]: ((general electric company).as.)AND((thermal barrier coating).ti.)

#	PATENT NO	TITLE	# CLAIMS	IND. CLAIMS
1	US-10995621-B2	Turbine airfoil with multiple walls and internal thermal barrier coating	20	1, 11, 15
2	US-10384978-B2	Thermal barrier coating repair compositions and methods of use thereof	40	1, 18
3	US-10221703-B2	Articles having damage-tolerant thermal barrier coating	14	1, 9
4	US-10179945-B2	CMAS resistant thermal barrier coatings	17	1
5	US-10100650-B2	Process for selectively producing thermal barrier coatings on turbine hardware	12	1, 11, 12
6	US-9657387-B1	Methods of forming a multilayer thermal barrier coating system	11	1
7	US-8510060-B2	Life management system and method for gas turbine thermal barrier coatings	18	1, 8, 13
8	US-7862901-B2	Yttria containing thermal barrier coating topcoat layer and method for applying the coating layer	16	1, 10
9	US-7807231-B2	Process for forming thermal barrier coating resistant to infiltration	19	1, 16
10	US-7666528-B2	Protection of thermal barrier coating by a sacrificial coating	9	1
11	US-7510777-B2	Composite thermal barrier coating with improved impact and erosion resistance	24	1, 11, 19, 22
12	US-7429424-B2	Sintering resistant, low conductivity, high stability thermal barrier coating/environmental barrier coating system for a ceramic matrix composite (CMC) article to improve high temperature capability	46	1, 12, 13, 37, 44, 46
13	US-7374825-B2	Protection of thermal barrier coating by an impermeable barrier coating	23	1, 22, 23

Part 1

Summary of 8 patents

- 1) This disclosure has 3 components: turbine airfoil, hot gas path (HGP) and manufacturing of the whole system (all variations). The may airfoil have multiple inner walls and all wall have a TBC coating. The main aim of this system is to provide a cooling effect or a heat sink. This is where the HGP component comes into picture. The airfoil (system) is made from additive manufacturing and a hot gas flows through the walls which are exposed to the heat. The TBCs protect the walls from the heat and keep them (relatively) cooler.
- 2) TBCs are continuously exposed to very high temperatures. Corrosion due to hot gases leads to crack formation and propagation. These cracks, if not mended in time, can lead to failure during operation. This patent introduces more methods of repairing as well as more types of compositions used for repair. The proposed methods can be performed on the object without removing it from its system.
- 4) A major application of TBCs is for coating turbine blades used in airplanes. At high altitudes, dust particles get heated to plasma state as they engage with the turbine system. They form molten glass

(CMAS) which leads to corrosion and deterioration. This patent discloses TBCs that are resistant to CMAS. It also discusses the composition stability of the new TBCs.

- 5) This patent provides a process of depositing TBCs on objects with different shapes and also removing unwanted deposits. This is a handy invention, as most of the widely used manufacturing processes are not much controlled. It is very difficult to selectively coat certain surfaces without coating others. This patent describes the process for individual coating layers within a TBC and how to remove coatings from obscure parts such as holes, curled edges etc.
- 7) TBCs are used for extending life of the substrate on which they lay, many time sacrificing their own wellbeing. This patent comes up with a digital twin-kind of product, which is used in process control and product life management. This tool can collect data, perform analysis and diagnose issues not only with the TBCs, but also with other components particularly found in turbines.
- 9) This patent discloses methods to deposit sacrificial/protective coating layers over TBCs. These new layers effectively deal with the CMAS corrosion and also withstand their composition through multiple heating and cooling cycles. The surface layer is made of particular elements whose oxides are able to effectively resist corrosion mechanism (spallation) occurring from hot gases.
- 12) This patent discloses a set of methods, object, and compositions for state-of-the-art Environmental Barrier Coatings (EBCs). This concept arises due to the need to protect the traditional TBCs from spallation due to hot gases, molten dust etc. The patent also excludes others from making, selling of a few components which are coated with EBCs. These objects are not commonplace, but particularly those used in turbine systems.
- 13) This patent excludes every other entity (except GEC) from using or developing TBCs that have rare earth silicates in the composition. The patent discloses method of depositing impermeable coatings over (then) conventional TBCs so as to prevent the important parts of both the TBCs and the substrate from spalling. It also discloses a composite which acts like the impermeable layer.

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Themes:

1 Quest of Finding New Material Compositions

Probably the most dominant theme in the chosen set of patents. Chemical composition is a tricky math, where properties change by incremental changes in composition, temperature, etc. Different amount of different elements mixed together might create a novel compound with properties never seen before. This is the area most prone to claim failure as well as easy to design around.

#	PATENT NO	TITLE	WHY
2	US-10384978-B2	Thermal barrier coating repair compositions and methods of use thereof	Talks about lots of ceramic compositions and temperature ranges for deposition. Also coat dimensions.
3	US-10221703-B2	Articles having damage-tolerant thermal barrier coating	Small patent, particularly for claiming new ceramic compound with mechanical and thermal characteristics.
4	US-10179945-B2	CMAS resistant thermal barrier coatings	Small patent, applying statistical (broad) limits on TBC material composition.
8	US-7862901-B2	Yttria containing thermal barrier coating topcoat layer and method for applying the coating layer	Small patent, disclosing novel anatomical structure of TBC, with vague (broad) bounds on material composition.
9	US-7807231-B2	Process for forming thermal barrier coating resistant to infiltration	Patents substrate compositions on which to deposit TBC. Written in very broad manner. Also explains the chemical process that would occur during the deposition.
10	US-7666528-B2	Protection of thermal barrier coating by a sacrificial coating	Small patent, describes particular phosphate composition to be used as sacrificial layer, which is the main claim of the patent.
11	US-7510777-B2	Composite thermal barrier coating with improved impact and erosion resistance	Describes composite material properties, fibre to matrix ratios, and mechanical properties.
12	US-7429424-B2	Sintering resistant, low conductivity, high stability thermal barrier coating/environmental barrier coating system for a ceramic matrix composite (CMC) article to improve high temperature capability	Describes crystal structure of metal oxide(s) along with fine details of compositions.
13	US-7374825-B2	Protection of thermal barrier coating by an impermeable barrier coating	Small patent, particularly excludes others from using a group of compounds for TBC.

2 Indirect Spotlight on Failure Mechanisms

These patents are cautious effort to prevent competitors or third parties in capturing the repairs market in TBCs. It shows systematic research towards failure mechanisms that provides knowledge to make or prevent repairs, also improve future coatings. This theme is evident after careful scrutiny of patent claims where indirectly solutions are disclosed to the failure mechanisms, without explicitly mentioning them.

#	PATENT NO	TITLE	WHY
2	US-10384978-B2	Thermal barrier coating repair compositions and methods of use thereof	Addresses basic crack failure by proposing compounds to patch the cracks.
3	US-10221703-B2	Articles having damage-tolerant thermal barrier coating	Discusses about 'more' resistance to infiltration.
4	US-10179945-B2	CMAS resistant thermal barrier coatings	Talks about 'soft' and 'tough' phases.
7	US-8510060-B2	Life management system and method for gas turbine thermal barrier coatings	This patent itself arises from the need to monitor the failure.
9	US-7807231-B2	Process for forming thermal barrier coating resistant to infiltration	Clearly discusses infiltration mechanism.
10	US-7666528-B2	Protection of thermal barrier coating by a sacrificial coating	Sacrificial coating to prevent further failure.
13	US-7374825-B2	Protection of thermal barrier coating by an impermeable barrier coating	Discusses 'more' adherent and impermeable coat.

3 Later Patents Inch Closer Towards Advanced Systems

GE has been in this field since long. After many years of research and filing abundant patents, the focus is bound to shift towards more advanced systems: built using components, processes, compositions or any feasible combination of these.

#	PATENT NO	TITLE	WHY
1	US-10995621-B2	Turbine airfoil with multiple walls and internal thermal barrier coating	Discusses complex substrate design on which a combination of any or all previous patented TBCs can be coated.
2	US-10384978-B2	Thermal barrier coating repair compositions and methods of use thereof	Talks about repairing 'damaged' regions.
3	US-10221703-B2	Articles having damage-tolerant thermal barrier coating	Makes careful effort to keep the design complex.
5	US-10100650-B2	Process for selectively producing thermal barrier coatings on turbine hardware	Combines compositions, substrate design and permutations of TBC layers.
10	US-7666528-B2	Protection of thermal barrier coating by a sacrificial coating	Patents any article (~job) to be coated with TBCs and for used in gas turbine engines.

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Question 1

*Please refer Appendix for highlighted portions

#	PATENT NO	EASIEST DESIGN AROUND	PART OF CLAIM
1	US-10995621-B2	Sandwiched walls Outlet valves The design is heavily broad around spaced walls, hence the exact opposite is the first obvious part. These walls need not be coated with TBCs. This is a frequent situation where two components come into contact with each other. The impingement openings can be argued against valves, that are 'controlled' openings or 'controlled blockages'.	Spaced walls Impingement openings providing passageways
2	US-10384978-B2	Around the damaged region *Lots of numbers can be chosen outside of the claimed range for chemical compositions. The chemical can be made to flow back into the central damaged region.	Onto the damaged region
3	US-10221703-B2	Thickness of outer layer is less than or equal to the thickness of the inner layer As stronger material from the outside will not need greater thickness.	Thickness of outer layer is greater than the thickness of the inner layer
4	US-10179945-B2	Splats created using controlled vapour deposition Eliminating the 'randomly' feature is feasible with accurate control.	Randomly distributed splats
5	US-10100650-B2	Aerodynamic component An airfoil is generally considered a subset of aerodynamic parts.	Airfoil component
6	US-9657387-B1	A coating chamber is a fancy name of the controlled space where plasma beams are used to deposit coats. TBCs are thin film coats (invisible). A process may be devised to create the film first and later move it onto the substrate using fusing methods.	Coating chamber
7	US-8510060-B2	Monitoring overall life and health Adds the lost useful life into consideration.	Predicting the remaining useful life

8	US-7862901-B2	74 wt% yttrium dioxide stabilised with minute traces of zirconia	75 wt% yttria
		Slight change in composition.	
9	US-7807231-B2	Oxide of substrate with one or more than one rare earth element.	Oxide of the at least one metal
		Such combinations of oxides are common in failure mechanism and hence easily found.	
10	US-7666528-B2	Magnesium phosphate, calcium phosphate, sodium phosphate and mixtures thereof	Magnesium phosphate, calcium phosphate and mixtures thereof
		Expand the set of compounds.	
11	US-7510777-B2	Around 5 micrometer	Greater than 5 micrometer
12	US-7429424-B2	Between 11 and 41 mol %	About 10 to about 40 mol %
		Covers all values between 10 and 40 including around 10 and around 40.	
13	US-7374825-B2	Sandwiched between	Adjacent to the
		Touches 1 walls from each side	

Question 2

Narrow claim: No. 2

Broader claim: No. 3

The constraints in patent 2 are a lot more than those in patent 3. This makes the claims in patent 2 more narrower. However, this does not infringe patent 3 as the mathematical ranges for yttria stabilized zirconia as described in the two patents are exclusive of each other. However, it is possible to argue that the mean diameters discussed in patent 2 will have to be designed around to file patent 3 after filing patent 2.

The claims in all other patents are neither overlapping nor very similar to each other, to argue about their patentability.

Part 2

New Product:

A new anatomy (structure) of a TBC in which multiple layers [multiplication] of rare earth oxides compositions are deposited on top of the substrate. Main difference being the alternate layers have a difference in the refractive indices [combine two opposites]. This way, the heat coming in radiation form will be reflected back to the surroundings at the junction of two adjacent layers. This type of coating can work against both conduction and radiation heat transfer [new advantage]. Although, radiation plays a slightly dormant role in applications where TBCs are being used; fractional increase in protection will still be advantageous in terms of fuel consumption, carbon footprint, and monetary investment.

*Innovation techniques highlighted (green)

Claim:

A thermal barrier coating (TBC) comprising of: multitude of any rare earth oxide layers deposited with either of physical vapor deposition and electron beam plasma film deposition over a functioning substrate (item) mainly used in aerospace applications; alternating pattern in multitude of any rare earth oxide layers having difference in refractive indices; thermally grown oxide (TGO) layers with thickness ranging from 2 um - 15 um pre-deposited at the contact plane of multitudes of any rare earth oxide layers.

Why is it valuable (broad enough)?

The claim talks about 'multitude of layers' thus can be customized. The substrate is associated with any part that is used in aerospace applications, thus a broad range of parts come under the 'substrate' definition. Alternate layers can have different refractive indices, regardless of how far the values are e.g. 2.000 and 2.001, 2 and 2000 are all covered. Most TGOs range between 2-15 um, so covered.

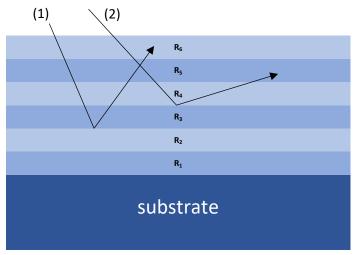
Why is it absolutely new (narrow enough)?

The novelty lies in alternating layers with different refractive indices, that is absolutely new. The substrate is constrained for aerospace components. TGOs are known to lie between the given thickness range, however that is on statistical basis and not a natural law. The range 2-15 provides a part of the bigger range where there is a up to 95% probability of growing a TGO during operation. The other concept which is absolutely new, is that the TGO is pre-deposited during manufacturing, without waiting for it to automatically appear during operation (as a result of ion exchange).

Description:

(1) Rare earth oxides are the choice for TBCs due to their unique mechanical and thermal properties. This invention makes use of an unaddressed material property which is an optical property, i.e. refractive index.

(2) The following diagram will be taken as reference for remaining discussion:



Diag. 1 Anatomy of Refractive TBC

- (1) incident ray at sharp angle
- (2) incident ray at large angle
- R_x refractive index
- (3) When materials with different refractive indices are put in contact of each other, electromagnetic rays get internally reflected and sometimes bounce back while crossing the interface. The rays bounce back when the angle of incidence is greater than the critical angle defined by ratio of the refractive indices of the two materials.
- (4) Rays incident from the hot surrounding, naturally flow towards the substrate (hot to cool). Along the way, with the new architecture, these rays gets reflected back due to change in refractive indices. The ratio of rays getting reflected with the ones getting transmitted forward depends on angle of incidence. E.g. ray (1) incident at a sharp angle may get deflected at one plane of contact, ray (2) incident at relatively large angle may get deflected at another plane of contact. This design, if customized based on statistical knowledge, can avoid almost all of radiation travelling to the substrate.
- (5) The inherent low thermal conductivity of the TBC layers will act continuously towards obstructing thermal conductance towards the substrate. Thus the continuous conductivity effect and alternative reflectivity effect act in tandem to reduce heat flow.
- (6) TGO layers can be deposited along the contact surfaces to avoid further corrosion layer formation during working. TGO layer composition can be chosen as combination of the two layers on either sides of the contact planes to maintain homogeneity. The refractive index of the TGO layer can also be engineered such that the two additional contact surfaces may also contribute towards radiation reflectance technology.

Part 3

Competitive Analysis			
#	Patent No	Previous Invention	Difference
1	US-10995621-B2	Turbine airfoil with multiple walls and internal thermal barrier coating	Does not have continuous array of TBC layers, one above the other
2	US-10384978-B2	Thermal barrier coating repair compositions and methods of use thereof	New invention is not about repairs or TBC compositions
3	US-10221703-B2	Articles having damage-tolerant thermal barrier coating	New invention is not about repairs or TBC compositions
4	US-10179945-B2	CMAS resistant thermal barrier coatings	New invention is not about corrosion resistance or TBC compositions
5	US-10100650-B2	Process for selectively producing thermal barrier coatings on turbine hardware	New invention is not about mfg. method
6	US-9657387-B1	Methods of forming a multilayer thermal barrier coating system	New invention is not about mfg. method
7	US-8510060-B2	Life management system and method for gas turbine thermal barrier coatings	New invention is not a life management system
8	US-7862901-B2	Yttria containing thermal barrier coating topcoat layer and method for applying the coating layer	New invention is not about mfg. method
9	US-7807231-B2	Process for forming thermal barrier coating resistant to infiltration	New invention is not about mfg. method
10	US-7666528-B2	Protection of thermal barrier coating by a sacrificial coating	The sacrificial coating is not a part of new invention
11	US-7510777-B2	Composite thermal barrier coating with improved impact and erosion resistance	New invention is not about composites and damage resistance
12	US-7429424-B2	Sintering resistant, low conductivity, high stability thermal barrier coating/environmental barrier coating system for a ceramic matrix composite (CMC) article to improve high temperature capability	New invention is not about composites and their properties

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13	US-7374825-B2	Protection of thermal barrier coating	New invention does use the
		by an impermeable barrier coating	basics from this invention, but
			adds more features to it

Appendix

§ Claim 1 of Selected Patents

1

A turbine airfoil, the turbine airfoil having a wall structure comprising: a plurality of spaced walls including an exterior wall, an intermediate wall, and an interior wall, wherein each of the plurality of spaced walls are separated from an adjacent spaced wall by a plurality of standoff members; a plurality of outer cooling chambers defined between the exterior wall and the intermediate wall; an outer partition between the exterior wall and the intermediate wall that axially separates each of the plurality of outer cooling chambers from one another; a plurality of intermediate cooling chambers defined between the intermediate wall and the interior wall; an intermediate partition between the intermediate wall and the interior wall that axially separates each of the plurality of intermediate cooling chambers from one another; a first thermal barrier coating (TBC) disposed on an exterior face of the exterior wall, the first TBC having an exterior surface configured to be exposed to a working fluid having a high temperature; a second TBC disposed on an outer face of the intermediate wall, the second TBC having an outer surface configured to be exposed to the working fluid having the high temperature; a first plurality of impingement openings through the interior wall, the first plurality of impingement openings providing passageways for a coolant from a central chamber of the turbine airfoil to at least one of the plurality of intermediate cooling chambers; a second plurality of impingement openings through the intermediate wall, the second plurality of impingement openings providing passageways for the coolant from at least one of the plurality of intermediate cooling chambers to at least one of the plurality of outer cooling chambers; and a plurality of cooling passages through the exterior wall, the plurality of cooling passages providing passageways for the coolant from at least one of the plurality of outer cooling chambers to the exterior surface of the first TBC.

2

A method for repairing a thermal barrier coating, wherein the thermal barrier coating is located on a component and wherein the thermal barrier coating has a damaged region, the method comprising: depositing a repair layer onto the damaged region, the repair layer comprising the repair composition comprising: a ceramic composition in an amount of from about 40 to about 60 percent by volume of the repair composition; a colloidal solution in an amount of from about 15 to about 25 percent by volume of the repair composition; an aqueous binder in an amount of from about 5 to about 15 percent by volume of the repair composition; an aqueous dispersant in an amount of from about 4 to about 8 percent by volume of the repair composition; an aqueous ammonia solution in an amount of from about 5 to about 10 percent by volume of the repair composition; wherein the ceramic composition comprises: a first population of yttria-stabilized zirconia particles having a mean diameter from about 250 nm to about 1000 nm, in an amount of from about 15 to about 30 percent by volume of the ceramic composition; a second population of yttria-stabilized zirconia particles having a mean diameter from about 2 µm to about 10 µm, in an amount of from about 10 to about 25 percent by volume of the ceramic composition; and a third population of yttria-stabilized zirconia particles having a mean diameter from about 20 µm to about 250 µm, in an amount of from about 50 to about 70 percent by volume of the ceramic composition; and wherein the colloidal solution comprises: an aqueous solvent in an amount of from about 90 to about 98 percent by volume of the colloidal solution; and a fourth population of yttria-stabilized zirconia particles having a mean diameter from about 2 nm to about 200 nm, in an amount of from about 2 to about 10 percent by volume of the colloidal solution; and heat treating the repair layer at a temperature of from about 900° C. to about

1400° C., to thereby form a patch, wherein the aqueous binder comprises water and a binder selected from the group consisting of poly(alkylene carbonate) copolymer, cellulose binder, poly(vinyl alcohol), and polyethylene glycol.

3

An article comprising: a plurality of coating layers disposed over a substrate, the plurality comprising an inner layer and an outer layer, wherein a) the outer layer comprises yttria-stabilized zirconia with an yttria content greater than 38 weight percent and is more resistant to infiltration by nominal CMAS relative to 8weight percent yttria-stabilized zirconia at a temperature of 1300 degrees Celsius; and b) the inner layer has, in a temperature range from about 1000 degrees Celsius to about 1200 degrees Celsius, a thermal resistance in a range from about 9×10 .sup.-5 degree Kelvin per watt to about 23 $\times 10$.sup.-5 degree Kelvin per watt, and a thickness of from about 200 to about 300 μ m, wherein a thickness of the outer layer is greater than the thickness of the inner layer.

4

A thermal barrier; coating comprising: a plurality of elongate material growth domains defined between domain boundaries, wherein the domains have an intra-domain density of at least about 75%, and comprise individual, randomly distributed splats of tough and soft phases stacked throughout the growth domains, and wherein the tough phases are at least one of partially stabilized zirconia compositions and partially stabilized hafnia compositions, and the soft phases are at least one of CMAS reactive compositions and CMAS resistant compositions, wherein at least about 75% of the splats of the domains include a width to length aspect ratio of greater than or equal to about 3:1.

5

A process comprising: depositing a bond coat on an airfoil component including on a trailing edge region thereof that defines a trailing edge of the airfoil component, within holes located within the trailing edge region and spaced apart from the trailing edge, and on lands located within the trailing edge region and between the holes; depositing a ceramic coating on the bond coat including on the trailing edge region of the airfoil component, within the holes located within the trailing edge region, and on the lands between the holes; and then selectively removing the ceramic coating within the holes without completely removing the ceramic coating on the trailing edge region and the lands between the holes and without completely removing the bond coat from the holes.

6

A method of forming a thermal barrier coating system on a surface of a component, the thermal barrier coating system comprising a thermal barrier coating that has columnar grains, the method comprising: introducing the component into a coating chamber, wherein a first ceramic source material and a second ceramic source material are positioned within the coating chamber of a physical vapor deposition apparatus; directing an energy source onto the first ceramic source material to vaporize the first ceramic source material to deposit a first layer on the component; alternating the energy source between the first ceramic source material and the second ceramic source material to form a blended layer on the first layer, wherein the blended layer is formed from vapors from the first ceramic source material and the second ceramic source material; and after alternating the energy source between the first ceramic source material and the second ceramic source material, directing the energy source onto the second ceramic source material to vaporize the second ceramic source material to deposit a second layer on the blended layer such that the blended layer is positioned between the first layer and the second layer.

7

A life management system for predicting the remaining useful life of a thermal barrier coating (TBC) of turbine hot gas and combustion components of a gas turbine unit, comprising: a nontransitory computer-readable storage medium comprising a series of computer instructions, for determining a cumulative damage of at least one component using operational data including temperature, the computer instructions comprising at least one damage transfer function based upon a physics model; the computer-readable storage medium further configured for determining a gas turbine unit risk and a classification probability; and a data fusion module that receives the cumulative damage of the at least one component and the gas turbine unit risk and classification probability, the data fusion module configured to calculate at least one life parameter including a thermal barrier coating parameter; wherein the at least one component comprises a thermal barrier coating.

8

A gas turbine engine component comprising: a superalloy substrate; a bond coat layer on the substrate; an adherent layer of ceramic material forming a thermal barrier coating on the bond coat layer, the thermal barrier coating comprising from about 4 wt % to about 8 wt % yttria stabilized zirconia; and a topcoat layer applied to the thermal barrier coating, the topcoat layer comprising greater than about 75 wt % yttria; wherein the topcoat layer includes a concentration gradient having an increasing concentration of yttria from the thermal barrier coating.

9

A process for forming a film on a thermal barrier coating that inhibits infiltration of porosity within the thermal barrier coating by a contaminant having a melting point of up to about 1225.degree. C. and containing oxides of calcium, magnesium, aluminum and silicon, the process comprising the steps of: applying to an outermost surface of the thermal barrier coating a deposited composition containing at least one metal chosen from the group consisting of aluminum and magnesium, the deposited composition being applied so as to form a deposited film that lies on the outermost surface of the thermal barrier coating and overlies the porosity within the thermal barrier coating beneath the outermost surface thereof; and then converting the metal within the deposited film so that the deposited film forms an oxide film containing an oxide of the at least one metal that resists infiltration of the contaminant into the thermal barrier coating, at least a portion of the oxide film forming a surface deposit on the outermost surface of the thermal barrier coating and overlying the porosity within the thermal barrier coating to close the porosity at the outermost surface of the thermal barrier coating and thereby serve as a barrier to infiltration of the contaminant into the porosity within the thermal barrier coating.

10

An article of manufacture for use in a gas turbine engine comprising: a part comprising a superalloy substrate having a surface covered with a ceramic thermal barrier coating; a sacrificial phosphate coating overlying the ceramic thermal barrier coating, wherein the sacrificial phosphate coating is selected from the group consisting of magnesium phosphate, calcium phosphate and mixtures thereof, wherein the sacrificial coating is present in an effective amount to react chemically with a calcium-magnesium-aluminum-silicon-oxide (CMAS) contaminant composition at an operating temperature of the thermal barrier coating to form a by-product material having a higher melting temperature or viscosity than the CMAS contaminant composition.

11

A component having a composite thermal barrier coating on a surface thereof, the composite thermal barrier coating consisting essentially of particles of an insoluble ceramic reinforcement material uniformly dispersed throughout grains having a matrix formed by a ceramic matrix material, the ceramic reinforcement material being chromia and having a yield strength greater than the ceramic matrix material at about 1100.degree. C., each of the particles of the ceramic reinforcement material having a maximum dimension, the average of the maximum dimensions of the particles being greater than five micrometers, the composite thermal barrier coating containing a sufficient amount of the ceramic reinforcement material to increase the impact resistance of the composite thermal barrier coating.

12

A thermal barrier coating in a thermal barrier coating/environmental barrier coating system (TBC/EBC system) located on a silicon containing material substrate, comprising a compound having a primary constituent portion and a stabilizer portion stabilizing said primary constituent, said primary constituent portion of said thermal barrier coating (TBC) consisting of a mixture of hafnia present in an amount of at least about 5 mol % of the primary constituent and zirconia, and said stabilizer portion of said thermal barrier coating comprises at least one metal oxide comprised of cations with a +2 or +3 valence present in the amount of about 10 to about 40 mol % of the thermal barrier coating, wherein the TBC compound has a cubic or a pycholore crystal structure.

13

A composite comprising a porous thermal barrier coating comprising stabilized zirconia on a metallic part selected from the group consisting of a Ni based and a Co based superalloy, and an impermeable barrier coating adjacent to the outer surface of the thermal barrier coating and forming an outer layer of the composite, wherein the impermeable barrier coating is dense and non-porous and comprises a rare earth silicate selected from the group consisting of a silicate of lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium and mixtures thereof, the impermeable barrier coating thereby preventing infiltration of a contaminant composition into the thermal barrier coating.