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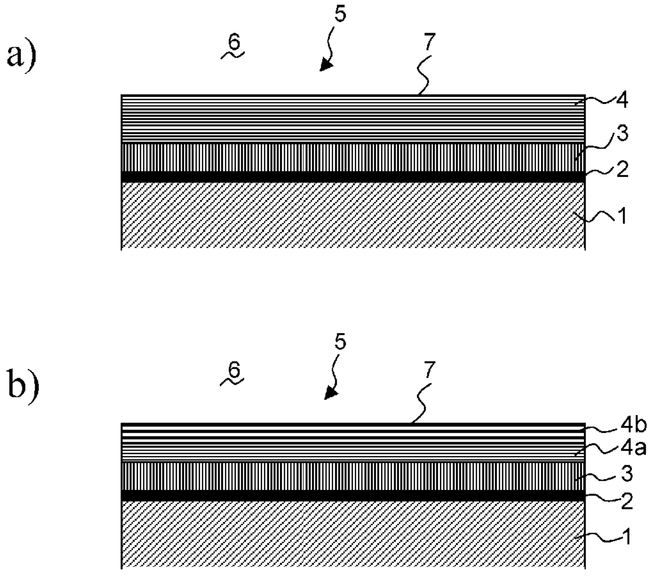
(54) Title: THERMAL BARRIER COATING SYSTEM, COMPONENTS COATED THEREWITH AND METHOD FOR APPLYING A THERMAL BARRIER COATING SYSTEM TO COMPONENTS

FIG. 1



(57) **Abstract**: A thermal barrier coating system (5) on a base material (1) is proposed comprising a bond coat layer (2) on its lower face in direct contact with said base material (1) and on its upper face in direct contact with a first ceramic layer (3). The thermal barrier coating system comprises further a second ceramic layer (4) on the outermost, hot gas exposed surface of the coating system. The first ceramic layer (3) consists of yttria- stabilised zirconia (ZrO_2) with a yttria content in the range of 6-8 wt-% (6w/o to 8w/o Y_2O_2), of $YTaO_4$ doped zirconia and/or titania doped zirconia. The material of the second ceramic layer (4, 4a, 4b) is selected from the group of: $YTaO_4$ doped zirconia, titania doped zirconia, scandia stabilised zirconia, ceria containing perovskite material, yttrium aluminium garnet material, Monazite material, spinel material, and combinations, mixtures, alloys, blends or multilayer structures thereof, with the proviso that if the first ceramic layer (3) consists of $YTaO_4$ doped zirconia and/or titania doped zirconia, the material of the second ceramic layer (4, 4a, 4b) is not selected from $YTaO_4$ doped zirconia and/or titania doped zirconia. Furthermore the invention relates to a method for applying such a thermal barrier coating system as well as two components provided with such a coating system.

TITLE

Thermal barrier coating system, components coated therewith and method for applying a thermal barrier coating system to components

TECHNICAL FIELD

The present invention relates to the field of thermal barrier coating (TBC) systems, in particular to multilayer YSZ-based coating systems, components coated therewith and to methods for applying such a thermal barrier coating system to components.

PRIOR ART

Up to now, TBC systems rely on a ceramic layer of yttria-stabilized zirconia deposited either by thermal spray (for instance atmospheric plasma spray) or by a vapor deposition method (like physical vapor deposition); deposited on a MCrAlY or a PtAl bondcoat which is deposited on the base material.

Up to now, the first choice TBC material is the 6-8 wt% yttria stabilized zirconia (YSZ) composition that was published by Stecura in US US 4,485,151. TBC prepared with 6-8 wt% yttria stabilized zirconia are after the coating process composed in the majority of a metastable tetragonal phase, which decomposes during exposure at high temperature. This decomposition process can lead to the destabilization and delamination of the TBC system.

During the past twenty years, numerous attempts have been performed at improving (TBC) systems.

Two main objectives have been targeted:

- Reduce the thermal conductivity of the TBC materials, such to allow a reduction of the cooling needs
- Increase the high temperature stability of the TBC materials, such to allow operating coated parts at higher surface temperature.

Both of these objectives are linked to a reduction of the cooling needs, which will be correlated with an increase of gas turbine efficiency.

During the first studies on improved TBC materials, the focus was on using zirconia-based materials and optimizing their doping such to obtain either an improved high temperature stability of the material or a reduced thermal conductivity.

In the context of the present invention of the following documents seem noteworthy:

US 4,335,190 discloses a multilayer system made of yttria stabilized zirconia with an inner layer which is around 1.5 pm thick. US 5,840,434 discloses a multilayer zirconia coating with an outer layer having a columnar structure. EP 0 605 196 discloses a multilayer zirconia coating with 0% porosity in the inner layer and 10-20& porosity in the outer layer. US 6,930,066 discloses a single layer zirconia coating stabilized with more than 30 wt% Y_2O_3.

EP1 514 953 discloses a multilayer zirconia coating with an outer layer consisting of cubic YSZ. US 6,887,595 discloses a multilayer system with an outer layer consisting of cubic zirconia stabilized with 1) Yb, Nd, Yb+La, Nd+La (5 to 49 mol %); 2) Y, Ca, Ce, Sc, Mg, In, (< 4 mole %); 3) Hf (0.5 to 40 mole %) or Ta (0.5 to 10 mole %).

US 4,328,285 discloses a single layer coating made of ceria stabilized zirconia. WO01/83851 discloses a multilayer system resistant to environmental contaminants, with an outer layer composed of ceria-stabilized zirconia, and the outer layer being significantly thinner than the inner layer.

US 6,812,176 and US 7,186,466 disclose a single layer coating made of zirconia stabilized with multiple cluster forming doping elements, the doping elements are for the majority rare-earths. EP 1 550 642 discloses a single layer coating made of YSZ (>91 mol%) + 1) Y, Ca, Ce, Sc, Mg, or In + 2) La, Gd, Nd, Sm, or Dy + 3) Yb or Er.

EP 1 550 645 discloses a single layer coating made of YSZ doped with La and Nd or doped with La and Yb. EP 1 627 862 discloses a coating made of Lanthana doped zirconia stabilized with one element from the group of Y, Gd, Ca, Ce, Mg, Sc, In. US 6,890,668 discloses a single layer coating made of (Er, Nd, Sm)-SZ having a cubic fluorite structure. EP 1 588 992 discloses a multilayer coating made of Hf-SZ doped with Y, Ca, Ce, Sc, Mg, In, La, Gd, Nd, Dy, Er, Yb, Eu or Pr.

US 4,913,961 discloses a single layer coating made of Sc-SZ.

US 4,335,190 discloses a multilayer system made of calcia-stabilized zirconia with an inner layer around 1.5 pm thick.

W00183851 (priority date 27.04.2000) discloses a multilayer system resistant to environmental contaminants, with an outer layer composed of calcia-stabilized zirconia, and the outer layer being significantly thinner than the inner layer.

EP 1 507 022 discloses a single layer coating made of YSZ doped with a pentavalent oxide which can be Ta (1-4 mol%).

US2002164430 discloses a single layer coating made of $CaZrO_3$ where Ca is partially substituted with another element like Sr.

EP 1 900 848 discloses a multilayer coating with an outer layer made of a material having a garnet structure, the coating will reduce sand related distress.

US 6,863,999 discloses a single layer coating of a rare-earth element phosphate (xenotime or monazite).

JP63274751 discloses a multilayer coating with an outer and inner layer system made of stabilized zirconia and the middle layer is composed of a spinel.

US 2006/0078750 discloses layer structures, in which, on a component, a first bond coat layer is applied and then a first ceramic layer consisting of 7YSZ. On this first ceramic layer there is provided a second ceramic layer. Among different possibilities, for the second ceramic layer multiple rare earth doped yttria stabilized zirconia is proposed. Analogous structures are disclosed in US 6887595 as well as in EP 1806435.

SUMMARY OF THE INVENTION

The object of the present invention is therefore to provide an improved thermal barrier coating system in particular for components which are exposed to hot corrosive gas flows, such as for example in the flow part of gas turbines, compressors and the like. Furthermore it is an object of the present invention to provide a method for producing such a thermal barrier coating system and to provide components coated at least in regions with such a thermal barrier coating system.

The object of the present invention is therefore a thermal barrier coating system according to claim 1, a process according to claim 14 and a component according to claim 15.

Specifically a thermal barrier coating system on a base material is proposed comprising a bond coat layer on its lower face in direct contact with said base material and on its upper face in direct contact with a first ceramic layer, and comprising a second ceramic layer on the outermost, hot gas exposed surface of the coating system. In other words on the base material, typically metal (including alloys), there is first a bond coat layer, followed by and in direct contact with the first ceramic layer, and then either directly follows the second ceramic layer forming the outermost hot gas exposed surface of the coating system or between this second ceramic layer and the first ceramic layer there is further intermediate layers. It should be noted that the second ceramic layer may also be over coated by some kind of impregnation or thin protective layer on its hot gas exposed surface. It should furthermore be noted that the first ceramic layer as well as the second ceramic layer may also be multilayer structures in which different materials or the same material is used. The expression "different materials" shall include materials with the same constituents (atoms) but in different proportions or different phases. Typically the first ceramic layer and the second ceramic layer is made of different materials.

According to the invention, the first ceramic layer consists of yttria-stabilised zirconia (ZrO_2) with a yttria content in the range of 6-8 wt-% (6w/o to 8w/o Y_2O_2).

Specifically, the yttria-stabilised zirconia (ZrO_2) with a yttria content in the range of 6-8 wt-% can be provided as described in US 4,485,151, and as concerns this possible material choice for the first ceramic layer, the disclosure of US 4,485,151 is specifically included into this disclosure.

In the alternative the first ceramic layer consists of $YTaO_4$ doped zirconia or of titania doped zirconia. It is also possible that the first ceramic layer consists of a combination (mixture and/or layers) of these differing materials. Preferably in case of $YTaO_4$ doped zirconia ZrO_2 is doped with 15 – 22 mol% $YTaO_4$.

According to the invention the material of the second ceramic layer furthermore is selected from one or several of the following materials:

$YTaO_4$ doped zirconia, titania doped zirconia, scandia stabilised zirconia, multiple rare-earth doped yttria stabilised zirconia, ceria stabilised zirconia, ceria containing perovskite material, yttrium aluminium garnet material, Monazite material (typically of the general structure $RE(PO_4)$ with RE = Ce, La, Nd, Pr, Y, may further comprise up to 20% Th), spinel material, and combinations, mixtures, alloys, blends or multilayer structures thereof.

The above definition of the materials for the first ceramic layer and the second ceramic layer is to be understood with the proviso that if the first ceramic layer consists of $YTaO_4$ doped zirconia and/or titania doped zirconia, the material of the second ceramic layer is not selected from $YTaO_4$ doped zirconia and/or titania doped zirconia. In other words the material for the first ceramic layer and for the second ceramic layer needs to be different in any case.

Up to now no TBC system did provide a significant improvement over the state of the art. One of the reasons of this lack of success has been proposed to reside in the combined effect of some YSZ properties:

1) Tetragonal zirconia exhibit a ferroelastic behavior that provide a toughening mechanism to the material;

2) Tetragonal zirconia can transform in monoclinic zirconia at low temperature and in cubic zirconia at high temperature. Any of these phase transformations lead to a

destabilization of the TBC and its failure. For this reason, tetragonal zirconia can be used in TBC only if it is the so-called non-transformable tetragonal region of the phase diagram, ranging from 6wt% Y203 doped ZrO_2 to around 12wt% Y_2O_3 doped ZrO_2. The toughening mechanism is considered to be important at the bondcoat-TBC interface, where the thermal stresses are the highest and usually the TBC failure occurs by cracking. The toughening mechanism provides a mechanism to slow down the crack propagation. At the outer surface of the TBC, the high temperature stability of the YSZ is critical for the TBC lifetime, since the temperatures that are experienced by the TBC induce a significant decomposition of the YSZ. The decomposition of the TBC forms a low yttria content phase which can transform from tetragonal to monoclinic upon cooling, and back to tetragonal upon heating. This phase transformation is accompanied by a volume change, which induces additional stresses in the TBC and can lead to its failure.

In the case of a multilayer TBC, the situation is different since one can use a material having good mechanical properties at the interface with the bondcoat and another material having high temperature stability for the outermost layer.

We thus propose a multilayer TBC system having a metal as base material (preferentially a Ni based superalloy), a bondcoat (preferentially a MCrAlY), a first ceramic layer of yttria-stabilized zirconia with 6-8 wt% of yttria or another material having a good toughening mechanism, and a second ceramic layer made of a material having an increased high temperature stability when compared to yttria stabilized zirconia with 6-8 wt% of yttria. As discussed above, the yttria-stabilized zirconia with 6-8 wt% of yttria layer allows to provide a toughening mechanism at the bondcoat-TBC interface, and the outer layer will reduce the current problems of the yttria-stabilized zirconia with 6-8 wt% of yttria decomposition at high temperature forming undesirable low yttria content tetragonal phase that will transform into a monoclinic phase upon cooling. Additionally the new TBC material can have a reduced sintering rate at high temperature. The TBC sintering leads to an increase of TBC stiffness, leading to an increased stress level in the TBC system and an increased the risk of TBC failure.

As mentioned above, the first ceramic layer preferably consists of $YTaO_4$ doped zirconia or of titania doped zirconia or of a combination (mixture and/or layers) of these differing materials. In this case the second ceramic layer can be selected from one or several of the following materials: $YTaO_4$ doped zirconia, titania doped zirconia, scandia stabilised zirconia, multiple rare-earth doped yttria stabilised zirconia, ceria stabilised zirconia, ceria containing perovskite material, yttrium aluminium garnet material, Monazite material (typically of the general structure RE(PO_4) with RE = Ce, La, Nd, Pr, Y, may further comprise up to 20% Th), spinel material, and combinations, mixtures, alloys, blends or multilayer structures thereof, again with the proviso that if the first ceramic layer consists of $YTaO_4$ doped zirconia and/or titania doped zirconia, the material of the second ceramic layer is not selected from $YTaO_4$ doped zirconia and/or titania doped zirconia. In other words the material for the first ceramic layer and for the second ceramic layer needs to be different in any case.

If the first ceramic layer consists of yttria-stabilised zirconia (ZrO_2) with a yttria content in the range of 6-8 wt-% (6w/o to 8w/o Y_2O_2), preferably the second ceramic layer is selected from one or several of the following materials: $YTaO_4$ doped zirconia, titania doped zirconia, scandia stabilised zirconia, ceria containing perovskite material, yttrium aluminium garnet material, Monazite material (typically of the general structure RE(PO_4) with RE = Ce, La, Nd, Pr, Y, may further comprise up to 20% Th), spinel material, and combinations, mixtures, alloys, blends or multilayer structures thereof, again with the proviso that if the first ceramic layer consists of $YTaO_4$ doped zirconia and/or titania doped zirconia, the material of the second ceramic layer is not selected from $YTaO_4$ doped zirconia and/or titania doped zirconia. In other words the material for the first ceramic layer and for the second ceramic layer needs to be different in any case. So preferably in this case the second ceramic layer does not comprise multiple rare-earth doped yttria stabilised zirconia, or ceria stabilised zirconia, In this respect it is specifically noted that the above-mentioned documents of the state-of-the-art, notably US 2006/0078750, US 6887595 as well as in EP 1806435 all only expressly disclose layer structures, in which, on a component, a first bond coat layer is applied and then a first ceramic layer consisting of 7YSZ, and on this specific first ceramic layer there is provided a second ceramic layer based on multiple rare earth doped yttria stabilized zirconia.

In a further preferred embodiment of the present invention, the base material is a metal, preferably a superalloy, more preferably a Ni-based superalloy. Generally, typical base materials as used in the hot gas path of gas turbines can form the base material for the thermal barrier coating system according to the invention.

According to a further preferred embodiment of the present invention, the bond coat layer comprises all preferably consists of a CrAl base material. Preferably it comprises or consists of MCrAlRX base material, wherein M is selected from Fe, Co, Ni or Co/Ni, R is selected from Y or Yb, and wherein X is optional and can for example be selected from Pt, Hf, Si, Zr, Ta, Re, and Ru and combinations thereof.

As mentioned above, according to a further preferred embodiment the second ceramic layer with its lower face directly contacts the (upper face of the) first ceramic layer, meaning that the first and the second ceramic layer are in direct contact with each other and there is no intermediate layers. For sufficient mechanical strength of the multilayer structure it is preferred that the interface between the two layers (first and second ceramic layer) is either graded or provided by a rough interface providing mechanical adhesion between the two layers.

The first as well as the second ceramic layer can be layer structures composed of several ceramic layers of course under the condition that the materials are selected as given above.

According to a further preferred embodiment however, the first as well as the second ceramic layer are single layers. The expression single layer shall mean that the whole layer is made of one same material (same phase, same composition/proportion of constituents). It is however not necessarily imply that the single layer is produced in a single deposition process, such a single layer may also be produced in a succession of deposition steps in which the same material is deposited in each step.

According to a further preferred embodiment, in particular second ceramic layer can be composed of at least two ceramic layers of different composition and/or microstructure and/or phase composition.

If for the first or the second ceramic layer $YTaO_4$ doped zirconia is used, preferably the zirconia is doped with 14-17 mol-% of $YTaO_4$.

If for the first or the second ceramic layer titania doped zirconia is used, the zirconia is preferably doped with 4-14 mol-% of TiO_2.

If for the second ceramic layer multiple rare-earth doped yttria stabilised zirconia is used, preferably the yttria doping is given by combinations of Nd/Yb, Gd/Yb, and/or Sm/Yb.

If for the second ceramic layer ceria stabilised zirconia is used, preferably the zirconia is doped with 20-30 mol-% of CeO_2.

If for the second ceramic layer ceria containing perovskite material is used, preferably this is selected from $BaCeO_3$ and/or $SrCeO_3$.

If for the second ceramic layer Monazite is used, preferably the Monazite this is selected as $LaPO_4$, optionally comprising Th.

If for the second ceramic layer a spinel is used, preferably this is selected from BaY2O4 and/or SrY_2O_4.

According to yet another preferred embodiment of the invention, the first ceramic layer has a porosity as measured according mercury porosimetry or by image analysis in the range of 10-40%, preferably in the range of 15-30%.

It is furthermore preferred that the first ceramic layer has a thickness in the range of 50-1000 μm, preferably in the range of 100-500 μm.

As concerns the second ceramic layer(s), it is preferred that it/they have/have a porosity in the range of 5-80%, preferably in the range of 5-25%.

The second ceramic layer(s) preferably has a graded porosity with a porosity in the range of 20-80%, preferably in the range of 20-25%, at the interface with the first ceramic layer and reducing to a porosity in the range of 5-20%, preferably in the range of 5-10% of the interface with the hot gas.

According to a further preferred embodiment, the second ceramic layer(s) has a thickness in the range of 300-2000 μm.

Furthermore it is generally preferred if the thickness of the first ceramic layer is smaller than the thickness of the second ceramic layer in case of a single second ceramic layer, and is smaller than the total thickness of the multitude of second ceramic layers in case of a multitude of second ceramic layers.

Furthermore the present invention relates to a method for making a thermal barrier coating system as described above.

Preferably the method is characterised in that in a first step (optionally after preceding surface preparation of the base material of metal such as grinding and/or cleaning and/or chemical treatment) a bond coat layer is applied to a component of metal base material. The bond coat layer is preferably applied by using thermal spray and/or electron beam physical vapour deposition. Subsequently in a second step the first ceramic layer is applied directly onto the bond coat layer in one or several steps. Preferably this ceramic layer is applied using a method selected from: electrophoretic deposition, plasma spray, electron beam physical vapour deposition, powder coating, vacuum powder spray deposition, chemical deposition, laser assisted deposition, ion beam assisted deposition. Now either intermediate ceramic layers can be applied and then the second ceramic layer applied, or, as preferred, the second ceramic layer is directly applied onto the first ceramic layer. Correspondingly in a third step the second ceramic layer or the several second ceramic layers are applied onto the first ceramic layer in one or several steps, optionally followed by the application of protective layer or protective impregnation of the surface. The methods for applying this second ceramic layer are preferably selected from one of the methods indicated above for the application of the first ceramic layer.

Furthermore the present invention relates to component, in particular hot gas exposed components of a gas turbine, comprising a coating system as described above, preferably produced using a method as described above.

Further embodiments of the present invention are outlined in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described in the following with reference to the drawings, which are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same. In the drawings,

Fig. 1 in a) is a schematic cut perpendicular to the surface plane of a component with a thermal barrier coating system with two ceramic layers; in b) as in a) but with three ceramic layers.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention consists of a multilayer TBC system having a metal base material 1, a bondcoat 2, a first ceramic layer 3 of yttria-stabilized zirconia with 6-8 wt% of yttria, and a second ceramic layer 4 made of any of the following materials:

- $YTaO_4$ doped zirconia (preferentially with 14-17 mol% $YTaO_4$);
- Titania doped zirconia (preferentially with 4-14 mo1% TiO_2);
- Scandia stabilized zirconia;
- A multiple rare-earth doped yttria stabilized zirconia (cominations of Nd & Yb, or Gd & Yb, or Sm & Yb);
- Ceria stabilized zirconia (preferentially with 20 to 30 mol% of CeO_2);
- A Ce containing perovskite material (preferentially $BaCeO_3$ or $SrCeO_3$);
- A yttrium aluminum garnet (YAG);
- Monazite ($LaPO_4$);
- A spinel (like BaY_2O_4 or SrY_2O_4).

Another possibility is to use a multilayer system as described above, but to change the composition of first ceramic layer using either titania doped zirconia, or $YTaO_4$ doped zirconia. Both of these compositions are expected to improve the toughness to the 1st ceramic layer 3. In this case the first ceramic layer 3 and the second ceramic layer 4 should not be composed of the same material.

As illustrated in figure 1 b, in particular the second ceramic layer 4 may comprise several layers of different material, indicated in the figure as 4a and 4b. These layers may have the same or different thickness. What is important is that the second ceramic layer 4 or the topmost of the second ceramic layers 4b is forming the surface 7 which is exposed to the hot gas flow 6. This however does not exclude that a thin surfacial layer can be present on the second ceramic layer, and also there may be impregnations on this top ceramic layer.

The interface between the first and second ceramic layers can be either graded (mixture of both materials with a composition gradient along the interface), or a rough interface providing also a mechanical adhesion between the two ceramic layers.

The first ceramic layer normally has a porosity level of 10-40% (preferentially from 15-30%) and a thickness of 50 to 1000 microns (preferentially from 100 to 500 microns).

The second ceramic layer can be composed of one or more ceramic layers of different microstructure or phase composition.

The second ceramic layer has a porosity level of 5-80% (preferentially 5-25%) and a thickness of 300 to 2000 microns.

The porosity level of the second ceramic layer can be graded starting from 20-80% (preferentially from 20-25%) at the interface with the 1" ceramic layer and reducing to 5-10% at the interface with the hot gas.

The bondcoat can be processed either by plasma spray or EB-PVD, and can be in some embodiment defined to have a specific composition.

In an experimental trial a prototype was produced by coating a base material 1 (specifically a component of a gas turbine) with a bond coat layer (composition by weight, see also US 6221181: 28-35% Co, 11-15% Cr, 10-13% Al, 0-1% Re, 1-2% Si, 0.2-1% Ta, 0.005-0.5% Y, 0-5% Ru, 0-1% Ca, 0-1% Mg, 0-0.5% La (or elements from the La series), 0-0.1% B, balance Ni and incidental impurities) using plasma spray deposition. The resulting thickness of the bond coat layer was in the range of 300-400 μm.

Subsequently a first ceramic layer of YSZ with the above specified yttria content was applied using thermal spray deposition leading to a layer thickness in the range of 300-500 μm and a first ceramic layer with a porosity of approximately 20-25 %.

After that second ceramic layer was deposited onto the rough top surface of the first ceramic layer using thermal spray deposition, wherein as a material $YTaO_4$ doped zirconia (14% doping in $YTaO_4$) was used. The resulting second ceramic layer had a layer thickness in the range of 600-800 µm and the second ceramic layer has a porosity of approximately 20-25 %.

Further experimental data for $YTaO_4$ in the first layer ($YTaO_4$ doped zirconia):

Samples were prepared by mixing ZrO_2 with 20 mol% of $YTaO_4$, after annealing at 1500°C for 600°C. The samples were investigated by means of X-Ray diffraction at room temperature, and no decomposition of the tetragonal $YtaO_4$-ZrO_2 phase is observed and no monoclinic ZrO_2 is observed (no dissociation of ZrO_2 and $YtaO_4$).

By contrast, in 7wt% Y_2O_3 stabilized ZrO_2 (/YSZ) samples, at such temperatures and annealing times the tetragonal phase is fully decomposed into cubic and monoclinic zirconia.

This is in agreement with data showing that with increasing $YTaO_4$ the transition temperature from tetragonal to monoclinic zirconia is reduced, allowing to retain a tetragonal zirconia structure down to room temperature.

Therefore ZrO_2 stabilized with 15-22 mol% $YtaO_4$ is an attractive TBC material, more specially at the interface between the bondcoat and the TBC, because of its:

1) long term stability at elevated temperature
2) absence of phase transformation upon heating and cooling
3) low thermal conductivity
4) high fracture toughness due to the ferroelastic behavior of the tetragonal zirconia phase

It has to be mentioned that in the Y-Ta-Zr-O system, there is normally only a small portion of the system (from ZrO_2 doped with 15mol% $YTaO_4$ to ZrO_2 doped with 22mol% $YTaO_4$) that is exhibiting the combination of this properties.

The resulting thermal barrier coating structure showed an increased resistance to spallation, delamination as well as destabilisation and showed ideal improved thermal conductivity values.

LIST OF REFERENCE SIGNS

1	base material, component
2	bond coat layer
3	first ceramic layer

4	second ceramic layer
4a	lower second ceramic layer
4b	surface second ceramic layer
5	thermal barrier coating system
6	area of hot gas flow
7	surface of 1

CLAIMS

1. Thermal barrier coating system (5) on a base material (1) comprising a bond coat layer (2) on its lower face in direct contact with said base material (1) and on its upper face in direct contact with a first ceramic layer (3), and comprising a second ceramic layer (4) on the outermost, hot gas exposed surface of the coating system, wherein the first ceramic layer (3) consists of the materials selected from the group of:
yttria-stabilised zirconia with a yttria content in the range of 6-8 wt-%,
of $YTaO_4$ doped zirconia,
titania doped zirconia,
and combinations, mixtures, alloys, blends or multilayer structures thereof; and wherein the material of the second ceramic layer (4, 4a, 4b) is selected from the group of:
$YTaO_4$ doped zirconia, titania doped zirconia,
scandia stabilised zirconia,
ceria containing perovskite material,
yttrium aluminium garnet material,
Monazite material,
spinel material,
and combinations, mixtures, alloys, blends or multilayer structures thereof
with the proviso that if the first ceramic layer (3) consists of $YTaO_4$ doped zirconia and/or titania doped zirconia, the material of the second ceramic layer (4, 4a, 4b) is not selected from $YTaO_4$ doped zirconia and/or titania doped zirconia.

2. Coating system according to claim 1, wherein the base material (1) is a metal, preferably a superalloy, more preferably a Ni-based superalloy.

3. Coating system according to any of the preceding claims, wherein the bond coat layer (2) consists of a PtAl base material and/or of a MCrAlRX base material, wherein M is selected from Fe, Co, Ni or Co/Ni, R is selected from Y or Yb, and wherein X is optional and can preferably be selected from Pt, Hf, Si, Zr, Ta, Re,

and Ru and combinations thereof.

4. Coating system according to any of the preceding claims, wherein the second ceramic layer (4) with its lower face directly contacts the first ceramic layer (3), wherein the interface between the two layers (3, 4) is either graded or provided by a rough interface providing mechanical adhesion between the two layers (3, 4).

5. Coating system according to any of the preceding claims, wherein the first as well as the second ceramic layer (4) are single layers.

6. Coating system according to any of the preceding claims, wherein the second ceramic layer (4) is composed of at least two ceramic layers of different composition and/or microstructure and/or phase composition.

7. Coating system according to any of the preceding claims, wherein
in case of $YTaO_4$ doped zirconia, the zirconia is doped with 14-17 mol-% of $YTaO_4$; and/or
in case of titania doped zirconia, the zirconia is doped with 4-14 mol-% of TiO_2; and/or
in case of ceria containing perovskite material, this is selected from $BaCeO_3$ and/or $SrCeO_3$; and/or
in case of Monazite, the material this is selected as $LaPO_4$, optionally comprising Th; and/or
in case of spinel, the material is selected from BaY_2O_4 and/or SrY_2O_4.

8. Coating system according to any of the preceding claims, wherein the first ceramic layer (3) has a porosity in the range of 10-40%, preferably in the range of 15-30%.

9. Coating system according to any of the preceding claims, wherein the first ceramic layer (3) has a thickness in the range of 50-1000 μm, preferably in the range of 100-500 μm.

10. Coating system according to any of the preceding claims, wherein the second ceramic layer(s) (4) has a porosity in the range of 5-80%, preferably in the range of 5-25%.

11. Coating system according to any of the preceding claims, wherein the second ceramic layer(s) (4) has a graded porosity with a porosity in the range of 20-80%, preferably in the range of 20-25%, at the interface with the first ceramic layer (3) and reducing to a porosity in the range of 5-20%, preferably in the range of 5-10% of the interface (6) with the hot gas.

12. Coating system according to any of the preceding claims, wherein the second ceramic layer(s) (4) has a thickness in the range of 300-2000 μm.

13. Coating system according to any of the preceding claims, wherein the thickness of the first ceramic layer (3) is smaller than the thickness of the second ceramic layer (4) in case of a single second ceramic layer, and is smaller than the total thickness of the multitude of second ceramic layers (4a, 4b) in case of a multitude of second ceramic layers.

14. Method for making a coating system according to any of the preceding claims, wherein in a first step bond coat layer (2) is applied to a component of metal (1), preferably by using plasma spray and/or electron beam physical vapour deposition, wherein in a second step the first ceramic layer (3) is applied onto the bond coat layer (2) in one or several steps, preferably by using a method selected from: thermal spray such as atmospheric plasma spray, vapor deposition, physical vapor deposition, electrophoretic deposition, plasma spray, electron beam physical vapour deposition, powder coating, vacuum powder spray deposition, chemical deposition, laser assisted deposition, ion beam assisted deposition, and wherein in a third step the second ceramic layer (4) or the several second ceramic layers (4a, 4b) are applied onto the first ceramic layer (3) in one or several steps, optionally followed by the application of protective layer or protective impregnation of the surface.

15. Component, in particular hot gas exposed components of a gas turbine, comprising a coating system according to any of claims 1-13, preferably produced using a method according to claim 14.

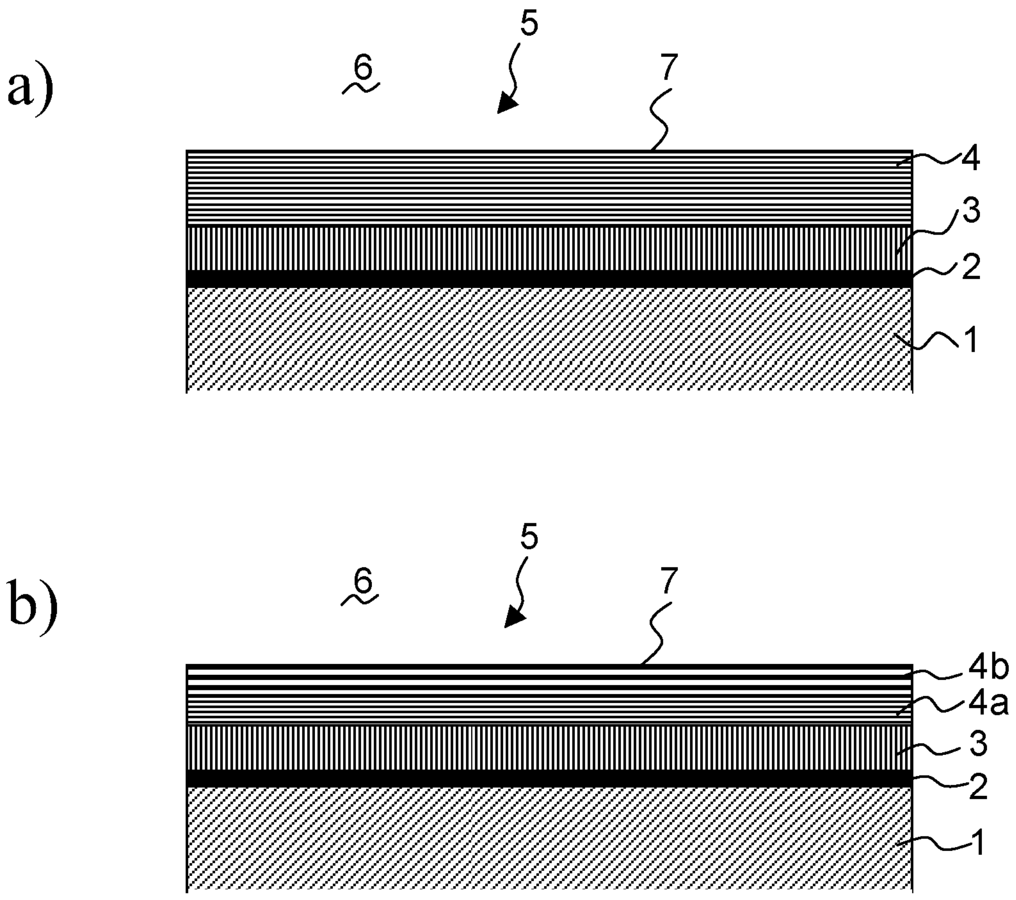


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067065

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C28/00 F01D5/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C F01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/078750 A1 (ZHU DONGMING [US] ET AL) 13 April 2006 (2006-04-13) paragraphs [0035], [0039]; claims 31,36-38	1-15
A	US 6 887 595 B1 (DAROLIA RAMGOPAL [US] ET AL) 3 May 2005 (2005-05-03) column 8, lines 20-58; examples 2,3	1-15
A	EP 1 806 435 A (GEN ELECTRIC [US]) 11 July 2007 (2007-07-11) paragraphs [0026] - [0031], [0039], [0041]	1-15
A	EP 1 900 848 A (UNITED TECHNOLOGIES CORP [US]) 19 March 2008 (2008-03-19) the whole document -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 15 January 2010	Date of mailing of the international search report 25/01/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Brisson, Olivier

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067065

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 514 953 A (FORSCHUNGSZENTRUM JUELICH GMBH [DE]) 16 March 2005 (2005-03-16) the whole document -----	1-15
A	WO 01/83851 A (STANDARD AERO LTD [CA]; SHANKER KARTIK [CA]) 8 November 2001 (2001-11-08) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/067065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006078750 A1	13-04-2006	NONE	
US 6887595 B1	03-05-2005	EP 1550743 A2	06-07-2005
		SG 112923 A1	28-07-2005
EP 1806435 A	11-07-2007	JP 2007182631 A	19-07-2007
		US 2007160859 A1	12-07-2007
EP 1900848 A	19-03-2008	SG 140539 A1	28-03-2008
		US 2008057326 A1	06-03-2008
EP 1514953 A	16-03-2005	NONE	
WO 0183851 A	08-11-2001	AT 321900 T	15-04-2006
		AU 5457501 A	12-11-2001
		CA 2306941 A1	27-10-2001
		DE 60118356 T2	07-12-2006
		EP 1276917 A1	22-01-2003
		ES 2261400 T3	16-11-2006
		HK 1052204 A1	25-08-2006
		JP 4221178 B2	12-02-2009
		JP 2003531966 T	28-10-2003
		JP 2008248393 A	16-10-2008
		US 2003138659 A1	24-07-2003