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(54) METHOD FOR MAKING HEAT BARRIER COATINGS

VERFAHREN ZUR HERSTELLUNG VON WÄRMEDÄMMSCHICHTEN

PROCÉDÉ DE FABRICATION DE REVÊTEMENTS DE BARRIÈRE THERMIQUE

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(56) References cited:
EP-A- 1 396 556 AU-A- 7 818 975
JP-A- 7 299 545 US-A- 5 897 921

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Description

[0001] The present invention relates to the development of a thick TBC coating, for application on gas turbine components, mainly on heat shields, combustion chambers and turbine wall covering panels, and the method for making it.

[0002] Nevertheless, protection is not only requested hereby for such application, but for any TBC deposition application, such as in the automotive industry (combustion engines).

[0003] The present invention relates to coatings, typically of ceramic material, deposited on a previously deposited layer used as a bond coat, said layers being obtained by Thermal Spray processes, such as:

- > Air Plasma Spray,
- > Vacuum Plasma Spray
- > High Velocity Oxygen Fuel

[0004] By decreasing the operating temperature of the components coated thereby, these coatings improve corrosion and heat-oxidation resistance of components, such as gas turbines and aeronautical engines.

[0005] US 5 897 921 discloses a method for making thick thermal barrier coatings according to the preamble of claim 1.

[0006] The above mentioned deposits may be, for instance, of a metal material obtained from a M-CrAlY alloy (where M means Ni, Co, Fe or a combination thereof) followed by yttria partially stabilized zirconia (YPSZ) coatings.

[0007] The process or method of deposition of thermal barrier coatings (TBC) divides ceramic coatings according to their thickness: thin TBCs are defined as coatings of a thickness from 200 to 800 μm , whereas thick TBCs are ceramic coatings of a thickness greater than 1 mm, generally in a range from 1,2 to 3 mm.

[0008] Particularly, the present invention relates to the particular method for depositing thick coatings, i.e. the particular handling/pivoting of the torch relative to the surface on which the coating has to be deposited, to obtain an improved coating microstructure as compared with currently available ones.

[0009] The present invention applies to both thick and thin coatings.

[0010] Furthermore, the structure so obtained improves resistance of the coating to thermal cycling fatigue (TFC), and thereby increases the performances of the components coated thereby (reduced operating temperatures and extended life of the component).

[0011] The principle of thermal spray technologies consists in supplying energy to the material to be deposited until it melts, and transfer it to the substrate to be coated. Energy may be supplied to the material to be deposited from various sources: energy deriving from combustion between oxygen and a fuel, either in gas form (propane, acetylene, hydrogen) or in liquid form

(kerosene) or deriving from recombination of ions in a plasma.

[0012] Thermal spray technologies include:

- Combustion Flame Spray,
- Arc Flame Spray,
- Plasma Spray,
- HVOF (High Velocity Oxygen Fuel).

[0013] The coating results from successive deposition of various numbers of layers which join together to form the coating (passes).

[0014] An important variable influencing the structure of the coating so obtained and consequently its performances is the tilt of the spray torch relative to the surface to be coated.

[0015] This invention provides a combination of successive tilts for the various passes that leads to an ideal coating structure: fine porosity with small pores evenly diffused over the coating structure.

[0016] The above objects and advantages are achieved by the method for making thermal barrier coatings according to this invention, which is characterized as set out in the annexed claims.

[0017] These and other features will be more apparent from the following description of a few embodiments, which are shown by way of example and without limitation in the accompanying drawings, in which:

- Figure 1 shows a component to be coated according to the present method, namely a part of combustion chamber
- Figure 2 shows the structure of a thermal barrier
- Figure 3 is an exemplary micrograph of the thermal barrier obtained by the present method, showing that porosity is variable
- Figure 4 is a schematic view of the system for thermal spray deposition of the coating, showing the changing angle of incidence of the torch relative to the surface to be coated.

[0018] Particularly referring to Figure 1, numeral 5 designates a component to be coated by TBC as described above; the component 5 may be part of a gas or aeronautical turbine.

[0019] In this case, the surface 3 is the one to be coated with the thick TBC.

[0020] Particularly referring to Figure 2, a thermal barrier coating system 11 according to the inventive specifications is shown, which barrier 11 is laid over the surface 3 of the component 5.

[0021] The thermal barrier coating system (TBC) 11 has a substrate 15 acting as a binder and/or a plurality of other layers designed for other possible purposes, such as: corrosion resistance, adhesion, diffusion barrier.

[0022] The substrate 15 is preferably deposited on the surface 3 of the component 5 using a conventional well-

known process.

[0023] Then, the coating 15 is deposited on said substrate 15 to act as a thermal barrier, using the method as described below.

[0024] Particularly referring to Figure 3, a possible microstructure of the thick TBC 13 is shown, as obtained by the coating method of the invention.

[0025] This microstructure has pores 23 of varying sizes according to the deposition technologies and the parameters being used.

[0026] Such porosities are characterized by a highly homogeneous arrangement, as ensured by the inventive deposition system.

[0027] The dispersion of the pores 21 and 23 is shown, whose number changes depending on the energy supplied during deposition. Therefore, the structure exhibits a variable porosity with fine pores evenly dispersed in the body of the coating obtained by the method of the present invention.

[0028] High ceramic cohesion areas 21 are also visible.

[0029] Referring to Figure 4, a schematic view of one of the combinations of the method for depositing the coating 13 is shown, which is carried out through successive passes at different angles of incidence of the torch 33.

[0030] During the tests, a cylindrical component to be coated was pivoted about its own axis and the torch was displaced over a rectilinear path along a straight line parallel to the axis of rotation of the component to be coated. The torch tilt relative to an ideal surface tangent to the one to be coated may be described as follows: the torch 33 carries out a first deposition step at a certain angle α relative to the surface 3 to be coated; then, the torch 33 is pivoted to such a position as to form a second angle of incidence β , other than α , to carry out another deposition step on the coating that has just been laid at a tilt angle α ; finally, the torch 33 is positioned/pivoted to form a third angle of incidence τ and a further deposition step is carried out.

[0031] The tests used the following angles τ , β and α .

- first pass at $45^\circ \pm 15^\circ$, [τ]
- second pass at $90^\circ \pm 15^\circ$, [β]
- third pass at $135^\circ \pm 15^\circ$, [α]

[0032] This 3-pass cycle with 3 tilts can be repeated a number of times until reaching the desired thickness.

[0033] While the example relates to a 3-pass cycle with 3 tilts, a different cycle may be provided.

[0034] A constant tilt pass may be repeated n times, which means that the cycle may include:

- n passes at tilt angle α
- n passes at tilt angle β
- n passes at tilt angle τ

[0035] Cycles like these have been tested.

[0036] The above cycle may be repeated a desired

number of times.

[0037] The succession of the various passes at different tilts provides a coating microstructure composed of fine pores evenly dispersed in the coating structure.

[0038] The number of pores increases with the energy used during the deposition.

[0039] The scope of the present invention encompasses both the mechanical component 1 (such as the gas or aeronautical turbine) having thick TBC coatings (typically of thicknesses from 0.8 to 3 mm) of ceramic material, such as yttrium oxide stabilized zirconia, obtained by a Thermal Spray process, deposited on the bond coat surface of the component, and the method for making it, in which the thermal coating 13 is obtained with three or more different tilts of the deposition torch 22, at different and well-defined angles relative to the surface to be sprayed.

[0040] These angles τ , β and α are preferably as follows:

- in a first pass $45^\circ \pm 15^\circ$, [τ]
- in a second pass $90^\circ \pm 15^\circ$, [β]
- in a third pass $135^\circ \pm 15^\circ$, [α]

[0041] Nevertheless, the order in which the torch 33 is tilted to form the various incidence angles τ , β and α for deposition of the coating within each cycle can change and different combinations from the above may be provided.

[0042] While reference has been specially made herein to three precise angles of incidence, the present method allows the head 33 to operate at angles in a range from 30° to 150° relative to the tangent to the surface 3 to be coated.

[0043] In the above coating cycle; the torch 33 is tilted at least at three different angles, by carrying out a deposition step for each of them, a required number of passes being performed for each angle.

[0044] The scope of the present invention obviously encompasses all the coatings obtained with the above method, for any substrate and component (not necessarily a part of a gas turbine or an aeronautical engine) coated with the TBC.

[0045] The coating 13 may be composed of zirconia, possibly stabilized with other materials (e.g. ceria, dysprosia, ytterbia, Ca or Mg oxide) or other ceramic materials (alumina, titania, spinels, perovskite, etc.).

[0046] The scope of the invention further encompasses the coating itself, obtained using the method described herein.

[0047] The invention as described herein provides an essential contribution to the thermal cycling fatigue resistance of TBC coatings, particularly thanks to the structure of the coating.

[0048] In ordinary industrial practice, the higher the porosity, the higher the thermal cycling fatigue resistance. Thanks to the present invention, thermal cycling fatigue resistance is obtained regardless of the porosity (from

11% to 28% in the tests).

[0049] By the present invention, four different porosity levels were obtained using the same structure with fine pores evenly dispersed over the coating body.

[0050] These structures are also within the scope of the invention, as they are obtained by the same method.

[0051] It shall be finally noted that the above deposition method applies to deposition of thermal barriers and of ceramic materials in general, regardless of the parameters being used to supply enough energy to the powder for such powder to be melted.

Claims

1. A method for making thick thermal barrier coatings (11), for use on gas turbine components (5) and mainly heat shields, combustion chambers or turbine wall covering panels, said thermal barrier coating (11) resulting from successive deposition of various numbers of layers (13, 15) which join together to form the coating (11), which coating (11) is obtained by any Thermal Spray process, **characterized in that** it includes the steps of laying at least three coating layers (13), each of said layers being deposited at a different angle (τ , β , α) of a spray torch (33); said angles (τ , β , α) being defined relative to the surface to be sprayed and covering a range from 30° to 150° with respect to the tangent to the surface (3) of the component (5) to be coated; the structure of said coating layers (13) exhibits a variable porosity with fine pores evenly dispersed in the body of the coating obtained.
2. A method as claimed in claim 1, **characterized in that** said angles (τ , β and α) are preferably 45° $\pm$ 15°, 90° $\pm$ 15° and 135° $\pm$ 15°; the order in which the torch (33) is tilted to form said angles (τ , β and α) of incidence can change to any combination whatever.
3. A method as claimed in claim 1, **characterized in that** the torch (33) performs one or more coating passes for each of said at least three angles.
4. A method as claimed in claim 1, **characterized in that** it can be repeated an arbitrary number of times.

Patentansprüche

1. Verfahren zur Herstellung von dicken thermischen als Schranken wirkenden Schichten, für die Verwendung auf Komponenten (5) von Gasturbinen und meistens thermische Schilder, Brennkammern oder die Wände von Turbinen bedeckende Tafel, wobei die gesagte als Schranke wirkende Schicht (11) von einer schrittweise Ablagerung verschiedener Men-

gen von Schichten (13, 15) resultiert, die zusammen-treffen um die Schicht (11) zu bilden, wobei die Schicht (11) aus irgendeinem Thermal Spray Prozess erhalten wird, **dadurch gekennzeichnet, dass** es folgende Schritte umfasst: Verlegung von mindestens drei bedeckenden Schichten (13), wobei jede von den gesagten Schichten mit einem verschiedenen Winkel (τ , β , α) einer Sprüh-Gebläse-lampe verlegt wird, wobei die gesagten Winkel (τ , β , α) mit Bezug auf die zu besprühende Oberflächen definiert sind, und einen Bereich von 30° bis 150° bedecken, mit Bezug auf die Tangente der Oberfläche (3) der zu überdeckenden Komponente (5); wobei die Konstruktion der gesagten bedeckenden Schichten (13) eine veränderliche Porosität aufweist, mit feinen gleichmässig im Körper der erreichten Schicht verteilten Poren.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die gesagten Winkel (τ , β , α) vorzugsweise 45° $\pm$ 15°, 90° $\pm$ 15° und 135° $\pm$ 15° betragen, wobei die Ordnung mit der die Gebläse-lampe (33) gedreht wird, um die gesagten Einfallwinkel (τ , β , α) zu bilden, mit irgendwelcher Kombination wechseln kann.
3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Gebläselampe (33) einen oder mehrere Durchgänge für jeden der gesagten mindestens drei Winkel.
4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** es um eine beliebigen Anzahl von Male wiederholt werden kann.

Revendications

1. Une méthode pour produire des revêtements thermiques à barrière (11) pour emploi sur des composants (5) de turbine à gaz, et surtout des protections thermiques, des chambres de combustion ou des panneaux de couverture des parois des turbines, le dit revêtements thermique à barrière (11) résultant d'une successive déposition de différents quantités de couches (13, 15) qui s'unissent ensemble pour former le revêtement (11), le dit revêtement (11) étant obtenu par quelconque procédé de Spray Thermique, **caractérisée en ce qu'elle** comprend les opérations de poser au moins trois couches (13) de revêtement, chacune des dites couches étant déposée avec un angle différent (τ , β , α) d'une torche spray (33); les dits angles (τ , β , α) étant définis en relation aux surface à arroser et couvrant un champ entre 30° et 150° en relation à la tangente à la surface (3) du composant (5) à revêtir; la structure des dites couches de revêtement montre une porosit  variable avec des pores fins dispers s r guli rement dans le

corps du revêtement obtenu.

2. Une méthode selon la revendication 1, **caractérisée en ce que** les dits angles (τ , β , α) sont préférablement de $45^\circ \pm 15^\circ$, $90^\circ \pm 15^\circ$ et $135^\circ \pm 15^\circ$; l'ordre avec le quel la torche (33) est tournée pour former les dits angles (τ , β , α) d'incidence peut varier selon une combinaison quelconque. 5
3. Une méthode selon la revendication 1, **caractérisée en ce que** la torche (33) fait un ou plusieurs passages de revêtement pour chacun des dits au moins trois angles. 10
4. Une méthode selon la revendication 1, **caractérisée en ce qu'**elle peut être répétée pour un nombre arbitraire de fois. 15

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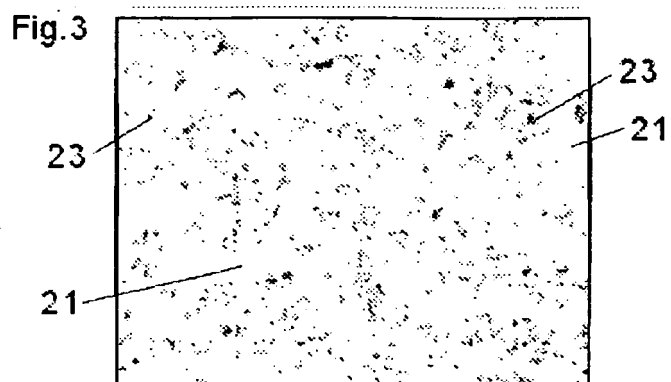
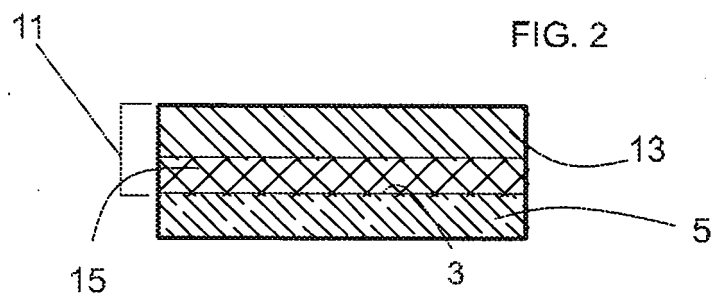
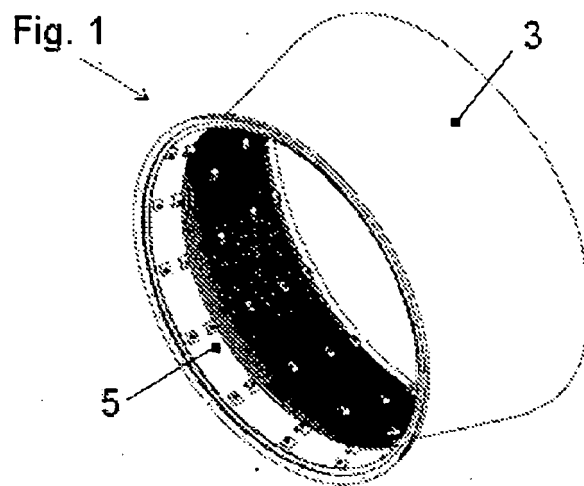
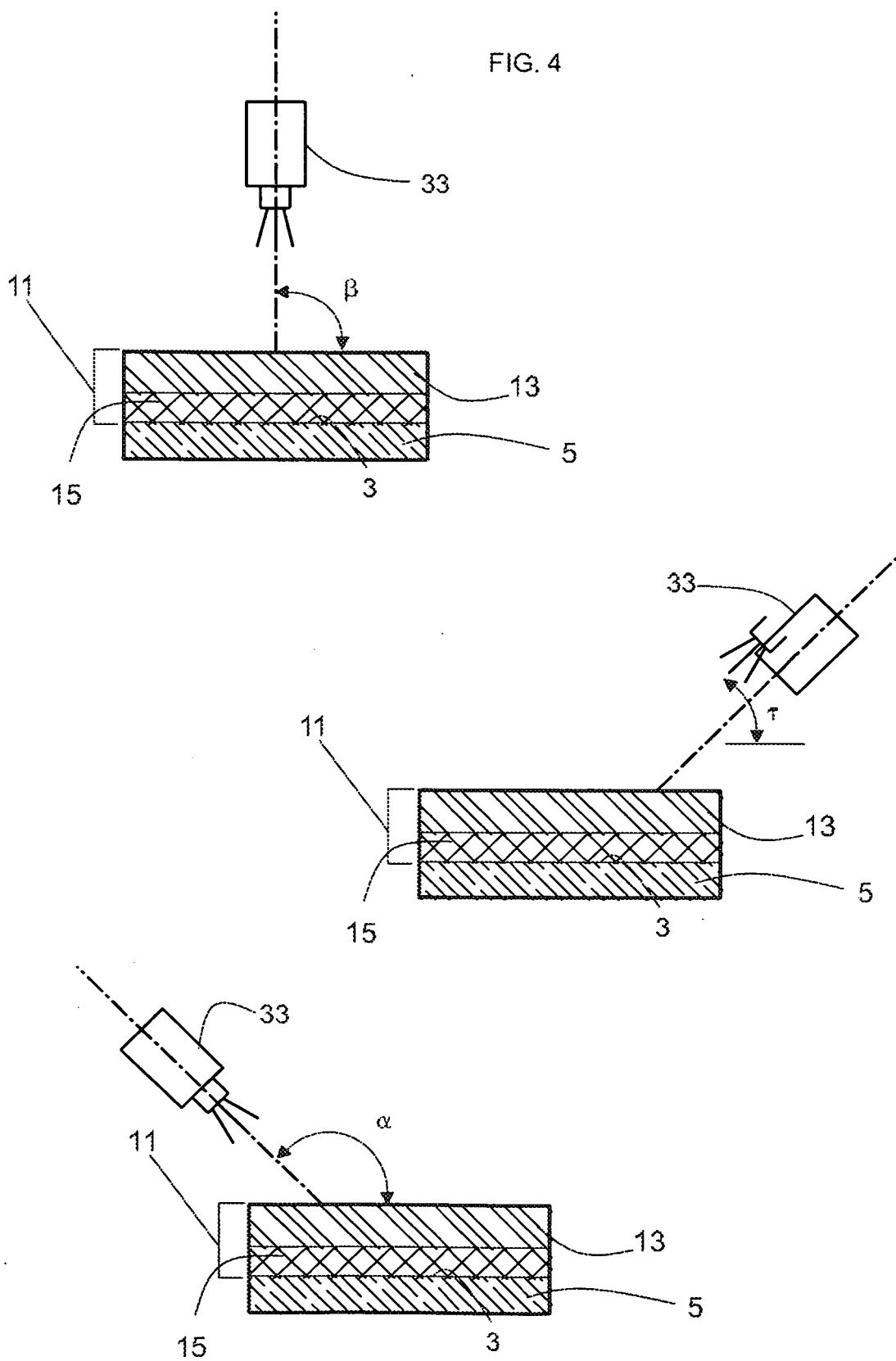


FIG. 4



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5897921 A [0005]