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(54) Method for smoothing the surface of a coating

(57) The present application refers to a method for reducing the roughness (Ra) of a first coating (1) with a defined coating composition and thermal expansion coefficient, said coating (1) covering the surface of a component (3) to be thermally high loaded, wherein in a first step the roughness (Ra) of said coating (1) is measured and in a following step a second slurry coating (2) is prepared for applying onto the surface of the first coating (1), whereby the coating composition of the second coating (2) is tailored to have a similar thermal expansion coefficient like the first coating (1). The method is characterized in calculating a minimum number of coating spray passes (N) necessary to provide the second slurry coating (2) with a thickness (T) that is at least two times of the roughness (Ra) of the first coating (1), then applying the slurry coating (2) with said calculated number of spray passes (N) onto the surface of the first coating (1), then fully curing, but only partially sintering the slurry coating (2) at a temperature in the range of 300 to 800°C and finally in polishing the second coating (2) to a reduced thickness (T') such that finally the second coating (2) does cover the first coating (1) only locally.

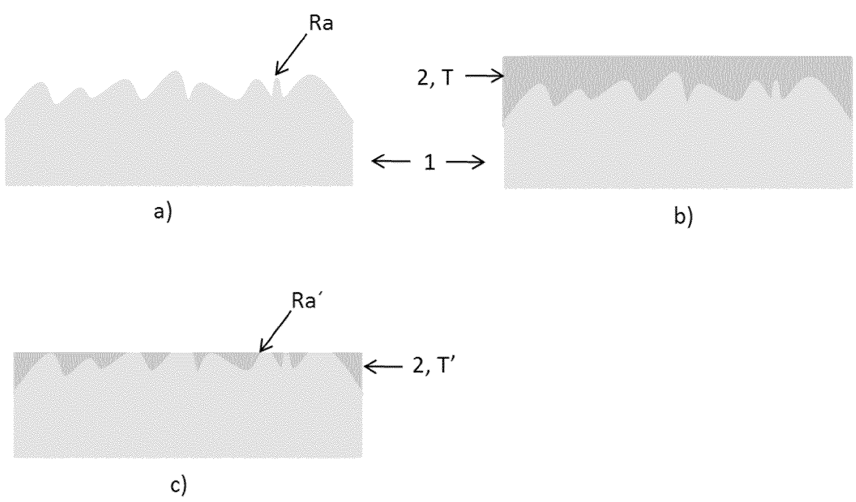

Fig. 2

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to coatings applied to metals and alloys. More specifically, the invention refers to a method for smoothing the rough surface of such coatings, especially thermal barrier coatings (TBC's) which are used for protection of thermal high loaded components, such as gas turbine blades, vanes or combustor parts.

PRIOR ART

[0002] Above mentioned surfaces of coatings exhibit a certain roughness. Within the meaning of the present application, smoothing the surface of the coating means that the roughness of said surface is reduced.

[0003] It is known state of the art to use TBC's for improvement of the performance of metallic components which are exposed to high temperatures.

[0004] Although gas turbine components are made of alloys, for example Ni-, Co- or Fe-based superalloys, which can resist high temperatures of more than 1000 °C there is a need for further increasing the operating temperature of the turbines to improve the efficiency of the gas turbines. This can be achieved among others for example by applying a thermal barrier coating onto the surface of the superalloy component. Most of the applied TBC's are ceramic-based coatings, preferably yttria-stabilized zirconia (YSZ). Such a material has a much higher temperature resistance than the above mentioned superalloys.

[0005] The TBC's are usually applied by thermal spray techniques, such as plasma spray processes like APS (Air/Atmospheric Plasma Spraying), VPS (Vacuum Plasma Spraying) or the very expensive EB-PVD (Electron Beam Physical Vapor Deposition).

[0006] APS technique is cheaper with respect to EB-PVD, but it has the disadvantage of a relative rough surface which can cause problems with respect to aerodynamic drag losses of appropriate coated gas turbine components. During operation of a gas turbine surface roughness increases turbulent heat transfer from the hot combustion gases to the component and thus reduces aerodynamic performance.

[0007] Therefore, several methods are used for smoothing the surface of the coatings, for example mechanical methods like grinding, polishing or sandblasting. Those methods can have the disadvantage of damaging the surface.

[0008] Additionally, the efficacy of the TBC is improved by introducing porosity in to the coating. However, when polishing the TBC, this inherent porosity will place a limit on the smoothness. The polishing process can open the closed pores.

[0009] Another method is described in document US 7368164 B2. A component used in a high-temperature environment, such as the combustor section of a gas turbine, is coated with a TBC made of yttria-stabilized zirconia, which provides the thermal protection for the substrate of the component. A bond coat, for example made of MCrAlY, is applied between the substrate and the TBC to promote adhesion of the TBC. The TBC is sprayed onto the bond coat by APS which results in a certain degree of inhomogeneity and porosity and in a rough surface of about 5-13 μm Ra. This leads to problems with respect to erosion resistance, transmissivity to infrared radiation and aerodynamic performance. To overcome these drawbacks the TBC is over-coated by a multilayer outer coating which is formed of two layers having different compositions. An inner layer of the coating contains alumina in a first silica-containing matrix material that is free of zinc titanate. An outer layer of the coating contains alumina, a glass material and zinc titanate in a second silica-containing matrix material. The thickness, structure and properties of the outer coating can be tailored by the firing temperature and durations used for each inner and outer layer. The outer layer of the coating has a low surface roughness Ra< 3 μm and forms the outermost surface of the component. As a result the new coating reduces the component temperature by reducing the convective and radiant heat transfer thereto. But the deposition of two different layers to the underlying TBC is expensive.

[0010] US 2007/0099013 A1 discloses also a method for manufacturing a TBC coated machine component, wherein a "smooth coat" ceramic layer is applied onto the component subsequent to the TBC. Because some of these smooth coat materials do not have a good adherence to the underlying TBC the smooth coat layer may spall during curing. To overcome the chipping of the smooth layer it is proposed in this document to deposit two TBC's, the outer thermal barrier coating having a higher porosity than the inner one, such to reduce the risk of delamination of the smooth coating layer. Such a solution is also cost intensive due to the necessity to deposit two different layers of TBC that means an additional layer of TBC is required.

[0011] Documents US 6294261 B1, EP 1088908 A2, EP 2236650 A1 describe further methods respective smooth slurry/gel layers or multilayer coatings to be deposited on a TBC. US 6294261 B1 and. EP 1088908 A2 disclose for example a slurry/gel composition which is based on yttria-stabilized zirconia as refractory filler and precursors of an oxide matrix, for example an alumina or an aluminosilicate matrix. The method for smoothing the surface of the protective coating (YSZ TBC) includes the steps of applying the slurry/gel to the TBC surface, heating the slurry/gel coating to remove volatile material and then further heating to cure the coating and bond it to the underlying protective coating. Using a slurry comprising zirconia means a good match of the thermal expansion coefficient of the TBC and the smooth layer. Matching the composition is a good way to reduce the thermo-mechanical stresses, but if the coating is too thick it will not prevent the formation of vertical cracks in the smooth layer. Unfortunately, such cracks reduce the aerodynamic efficiency of the smooth coating reducing the benefit of the coating.

[0012] The challenge according to those documents is to provide a smooth layer that has a low roughness (Ra< 6 μm, preferentially <3 μm) without reducing the lifetime of the underlying thermal barrier coating. The roughness that can be achieved with the smooth layer is strongly affected by the layer porosity. Therefore a low porosity in the coating prior to polishing (< 1 %) is necessary. At low coating porosity the coating is stiff with a high Young's modulus. Due to this high modulus, thermo-mechanical stresses linked to the difference in the coefficient of thermal expansion between the smooth layer and the underlying TBC can be sufficient to induce cracking in one or both coatings. Depending on the coating architecture this can lead either to early TBC spallation or to smooth layer chipping and reduction of the aerodynamic performance.

SUMMARY OF THE INVENTION

[0013] It is an object of the present invention to provide an effective and cost-efficient method for smoothing the surface of a coating that means reducing the roughness Ra of a coating, preferable a ceramic TBC which is applied to a high thermally loaded gas turbine component made of a superalloy.

[0014] It is another object of the invention to disclose an appropriate smooth coating system itself, preferably comprising a TBC which is used for protection of gas turbine components and which improves the aerodynamic behavior and therefore increases the turbine efficiency and which is able to minimize the thermo-mechanical stresses.

[0015] These and other objects are obtained by a method according to claim 1 and a coating system according to claim 8 resp. 9.

[0016] The disclosed method for reducing the roughness of a first coating with a defined coating composition and a thermal expansion coefficient, said coating covering the surface of a component to be thermally high loaded, comprises that

- in a first step the roughness of said coating is measured and
- in a following step a second slurry coating is prepared for applying onto the surface of the first coating, whereby the coating composition of the second coating is tailored to have a similar thermal expansion coefficient like the first coating. The method is characterized in
- calculating a minimum number of coating spray passes necessary to provide the second slurry coating with a thickness that is at least two times the surface roughness of the first coating;
- applying the slurry coating with said calculated number of passes onto the surface of the first coating;
- fully curing, but only partially sintering the slurry coating at a temperature in the range of 300 to 800 °C and
- polishing the second coating to reduce the thickness such that finally the second coating does cover the first coating only locally.

[0017] The last mentioned step is done by polishing the slurry down to the point where the "peaks" in the underlying TBC roughness are at the surface (visibly), and only the "valleys" in the TBC roughness remain filled with slurry coating.

[0018] With such a technical solution a dense, thin coating for a smooth layer can be provided to minimize the thermo-mechanical stresses using a cost effective manufacturing process. Minimizing the smooth layer thickness and polishing it such that the smooth layer (= second coating) does not cover 100 % of the first coating surface after smoothening it, leaving some areas where the first coating is appearing.

[0019] To achieve such a low smooth layer thickness without requiring a long time and cost consuming polishing process, the coating has to be manufactured such that it is dense, fully cured but only partially sintered to avoid too much recrystallization of the filler material. In this state the slurry coating can be described as a "machinable ceramic".

[0020] According to an embodiment of the invention the curing resp. partially sintering of the slurry coating is done at a temperature in the range of 500 to 800 °C.

[0021] It is an advantage applying a zirconia based slurry coating with a small amount of alumina silicate or zirconium silicate. The zirconia can be un-stabilized or preferably stabilized, more preferably stabilized with Y_2O_3, CaO, MgO or any combinations thereof. The slurry coating binder can be a silicate solution, phosphate solution or silicon emulsion. The first coating is a ceramic thermal barrier coating (TBC), preferably made of chemically stabilized zirconia. By using those materials it is realized that the thermal expansion coefficients of both coatings are close to each other.

[0022] The described method is especially effective for coating systems where the first coating is applied by atmospheric plasma spraying and has therefore a relative high roughness and high porosity, which can cause the above described disadvantages, for example reduction of aerodynamic performance.

[0023] The disclosed coating system for surface protection of a thermally high loaded component which is produced with a method according to claims 1 is characterized in that the coating system consists of a first underlying coating and a second slurry coating overlaying the first coating, wherein both coatings (1, 2) have a chemical composition with a similar thermal expansion coefficient, and wherein the second coating is very dense with a porosity < 1%, fully cured, but only partly sintered and wherein the second coating does only cover locally the first coating, so that said coating system finally comprises a reduced roughness with respect to the roughness of the originally applied first coating.

[0024] It is an advantage if the coating system for surface protection of a thermally loaded component has a second coating which is only completely sintered as a result of the first firing in the engine.

[0025] Specifically, the disclosed coating system is applied onto the surface of a gas turbine component made of a Ni-, Co-, Fe-based superalloy or combinations thereof, wherein the first coating is a ceramic thermal barrier coating, preferably made of chemically stabilized zirconia and the second coating is made by applying of a zirconia based slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] The present invention is now to be explained more closely by means of different embodiments and with reference to the attached drawings.

Fig. 1 shows a typical cross section of a TBC as first coating and a very thin smooth layer (second coating) according to an embodiment of the present invention;

Fig. 2 shows schematically the results after different steps (2a-2c) of the disclosed method;

Fig. 3 shows the surface of a coating in service in form of a photo, when the coating is too thick (prior art) and

Fig. 4 shows the surface of a coating in form of a photo, where the coating was manufactured according to the present invention.

DETAILED DESCRIPTION OF DIFFERENT EMBODIMENTS OF THE INVENTION

[0027] The present invention is related to coatings applied to metals and alloys. More specifically, it refers to a method for smoothing the rough surface of such coatings, especially thermal barrier coatings (TBC's) which are used for protection of thermal high loaded components, such as gas turbine blades, vanes or combustor parts.

[0028] TBC's especially applied by atmospheric plasma spraying methods onto the surface of above mentioned components have a relative high roughness. For improving the aerodynamic behavior which allows increasing the turbine efficiency it is necessary to provide a smooth surface layer by an efficient method which is cheaper and faster with respect to the known methods in the prior art. Additionally, to improve perform in-service the smooth surface layer needs to be thinner.

[0029] The present application discloses a method for reducing the roughness Ra of a first coating 1 with a defined coating composition and a thermal expansion coefficient, said coating 1 covering the surface of a component 3 to be thermally high loaded, the method comprises that in a first step the roughness of said coating 1 is measured and in a following step a second slurry coating 2 is prepared for applying onto the surface of the first coating 1, whereby the coating composition of the second coating 2 is tailored to have a similar thermal expansion coefficient like the first coating 1. The method is characterized in

- calculating a minimum number of coating spray passes N necessary to provide the second slurry coating 2 with a thickness T that is at least two times of the roughness of the first coating 1,
- applying the slurry coating 2 with said calculated number of spray passes N onto the surface of the first coating 1;
- fully curing, but only partially sintering the slurry coating 2 at a temperature in the range of 300 to 800 °C and
- polishing the second coating 2 to a reduced thickness T' such that finally the second coating 2 does cover the first coating 1 only locally (i.e. The "valleys" in the underlying TBC roughness are filled with dense slurry.).

[0030] With such a technical solution a dense coating 2 for a smooth layer can be provided to minimize the thermo-mechanical stresses using a cost effective manufacturing process. Minimizing the smooth layer thickness T and polishing it to a reduced thickness T' such that the smooth layer (= second coating 2) does not cover 100 % of the first coating's 1 surface after smoothening it, leaving some areas where the first coating 1 is appearing.

[0031] To achieve such a low smooth layer thickness without requiring a long time and cost consuming polishing process, the coating has to be manufactured such that it is dense, fully cured, but only partially sintered to avoid too much recrystallization of the filler material.

[0032] According to an embodiment of the invention the curing resp. partially sintering of the slurry coating is done at a temperature in the range of 500-800 °C.

[0033] Fig. 1 shows a photo of the microstructure (cross section) of a typical TBC 1 with a smooth layer 2 on the top according to one embodiment of the invention, where the desired reduction in surface roughness is achieved. The smooth layer 2 is very thin to the extent that the slurry fills the "valleys" in the underlying TBC roughness.

[0034] The "peaks" in the underlying TBC roughness are not covered by the slurry coating. The slurry is in the "valleys" of the underlying TBC roughness. The "peaks" in the underlying TBC roughness are not covered by the slurry coating.

[0035] The embodiment in Fig. 1 is a component produced with the method according to the present disclosure. The component is made of Hastelloy X base material. It has an APS MCrAlY bond coat. The TBC (first coating 1) is APS 7 wt% yttriastabilized zirconia. The slurry coating (second coating 2) is un-stabilized zirconia with the addition of a small amount of alumina silicate. The slurry coating binder was a water based silicon emulsion. The average initial TBC roughness Ra was 17.2μm. The average initial TBC thickness was 941μm, measured non-destructively with eddy-current equipment. The slurry coating was applied with a commercial paint sprayer. The number of spray passes N was 6. The eddy-current thickness measurements of the as sprayed slurry plus the TBC had an average value of 982 μm, thus the average slurry coting 2 thickness T was 41μm. The slurry was cured at 700°C for 5h. After curing the slurry coating 2 was polished with a fine grit wet silicon-carbide paper. After polishing the finial average roughness Ra' was found to be 2.8 μm. The non-destructive eddy-current thickness measurements of the as smooth layer plus the TBC had an average value of 945 μm. From the cross section photos the deepest slurry filed "valley" depth was 21μm.

[0036] The partially sintered slurry coating 2 is inherently softer than the TBC coating 1. During the beginning of polishing of the softer slurry coating, the abrasion rate is relatively high. As the slurry coating becomes thinner and the tops of the harder TBC "peaks" in the roughness are reached the polishing abrasion rates slows and even stops. Thus leaving only the TBC "valleys" in the roughness are filled with the slurry coating.

[0037] It is an advantage applying a zirconia based slurry coating with a small amount of alumina silicate or zirconium silicate. The zirconia can be unstabilized or stabilized with Y_2O_3, CaO, MgO or any combinations thereof. The slurry coating binder can be a silicate solution, phosphate solution or silicon emulsion. The first coating is a ceramic thermal barrier coating (TBC), preferably made of chemically stabilized zirconia. By using those materials it is realized that the thermal expansion coefficients of both coatings are close to each other.

[0038] The described method is especially effective for coating systems where the first coating is applied by atmospheric plasma spraying and has therefore a relative high roughness, which can cause the above described disadvantages, for example reduction of aerodynamic performance.

[0039] The disclosed coating system or surface protection of a thermally high loaded component which is produced with a method according to claims 1 is characterized in that the coating system consists of a first underlying coating and a second slurry coating overlaying the first coating, wherein both coatings 1, 2 have a chemical composition with a similar thermal expansion coefficient, and wherein the second coating is very dense with a porosity < 1%, fully cured, but only partly sintered and wherein the second coating does only cover locally the first coating, so that said coating system finally comprises a reduced roughness with respect to the roughness of the originally applied first coating.

[0040] It is an advantage if the coating system for surface protection of a thermally loaded component has a second coating which is only completely sintered as a result of the first firing in the engine.

[0041] Specifically, the disclosed coating system is applied onto the surface of a gas turbine component made of a Ni-, Co-, Fe-based superalloy or combinations thereof, wherein the first coating is a ceramic thermal barrier coating, preferably made of chemically stabilized zirconia and the second coating is made by applying of a zirconia based slurry.

[0042] Fig. 2 shows schematically the results after different steps of the disclosed method.

[0043] Fig. 2a shows the first coating 1 prior to the applying of the second coating - the high roughness Ra is clearly to be seen, it is about 8-18 μm.

[0044] Fig. 2b shows the system with the first coating 1 and the applied second coating 2. The roughness of the first coating Ra is the same like in Fig. 2a, but the overlying coating 2 may provide a smooth surface however it is too thick (with an average thickness T≥2xRa) and may crack during serves.

[0045] Fig. 2c shows the result after the last step of the described method according to claim 1. The coating system comprises the first coating 1 with the second coat 2 and a reduced roughness Ra' (which is about 1-6 μm) with respect to the originally applied coating 1. The reduced thickness T' of the second coating 2 is T'≈ Ra, such that finally the second coating 2 does cover the first coating 1 only locally.

[0046] According to an embodiment of the invention, the number of spray passes N, the thicknesses T, T' and roughness Ra, Ra' are coupled, by approximately N ≥ T/R (with R= deposition rate for one spray pass N), T ≥ 2xRa, after smoothing T' ≈ Ra, which may require optimizing for special composition and coating equipment.

[0047] Fig. 3 shows in a photo the surface of a coating in service, when the smooth surface coating is too thick (prior art). A lot of undesired cracks can be recognized.

[0048] In contrast to Fig. 3 Fig. 4 shows in a photo the surface of a coating system manufactured according to the present invention. The dark spots are the TBC appearing at the surface after the polishing step. Microcracks / cracks can't be recognized. The dark spots are the "peaks" in the underlying TBC roughness appearing at the surface.

[0049] The durability of the coating is ensured, providing improved aerodynamic performance over a long period of operation. There is also no thermal barrier coating lifetime reduction due to the smoothened surface.

List of reference numerals

[0050]

1	first coating, preferably TBC
2	second coating, slurry coating
3	thermally loaded component, for example gas tur-

bine blade

4	coating system
Ra	roughness of the surface (of the first coating 1)
Ra'	reduced final roughness of the surface
T	thickness of pos. 2
T'	reduced thickness of pos. 2
N	number of coating spray passes for pos. 2
R	deposition rate for one spray pass

Claims

1. Method for reducing the roughness (Ra) of a first coating (1) with a defined coating composition and thermal expansion coefficient, said coating (1) covering the surface of a component (3) to be thermally high loaded, wherein in a first step the roughness (Ra) of said coating (1) is measured and in a following step a second slurry coating (2) is prepared for applying onto the surface of the first coating (1), whereby the coating composition of the second coating (2) is tailored to have a similar thermal expansion coefficient like the first coating (1); **characterized in**

- calculating a minimum number of coating spray passes (N) necessary to provide the second slurry coating (2) with a thickness (T) that is at least two times of the roughness (Ra) of the first coating (1),
- applying the slurry coating (2) with said calculated number of spray passes (N) onto the surface of the first coating (1);
- fully curing, but only partially sintering the slurry coating (2) at a temperature in the range of 300 to 800 °C; and
- polishing the second coating (2) to a reduced thickness (T') such that finally the second coating (2) does cover the first coating (1) only locally.

2. Method according to claim 1, **characterized in** curing resp. partially sintering the slurry coating (2) at a temperature in the range of 500 to 800 °C.

3. Method according to claim 1, **characterized in** applying a zirconia based slurry coating (2) with alumina silicate or zirconium silicate additives and a slurry coating binder being a silicate solution, phosphate solution or silicon emulsion.

4. Method according to claim 3, **characterized in that** the zirconia is stabilized with Y_2O_3, CaO, MgO or any combinations thereof.

5. Method according to claim 1, **characterized in that** the first coating (1) is a ceramic thermal barrier coating (TBC), preferably made of chemically stabilized zirconia.

6. Method according to claim 1, **characterized in** applying the first coating (1) by atmospheric plasma spraying.

7. Method according to one of the claims 1 to 6, **characterized in** completely sintering the second coating (2) only after the first exposition to thermal loaded operation of the component (3).

8. Coating system (4) for surface protection of a thermally high loaded component (3) which is produced with a method according to one of the claims 1 to 6, **characterized in that** the coating system (4) consists of a first underlying coating (1) and a second slurry coating (2) overlaying the first coating (1), wherein both coatings (1, 2) have a chemical composition with a similar thermal expansion coefficient, and wherein the second coating (2) is very dense with a porosity < 1%, fully cured, but only partly sintered and wherein the second coating (2) does only cover locally the first coating (1), so that said coating system (4) comprises a reduced roughness (Ra') with respect to the roughness (Ra) of the originally applied first coating (1).

9. Coating system (4) for surface protection of a thermally loaded component (3) which is produced according to claim 7, **characterized in that in that** the coating system (4) consists of a first underlying coating (1) and a second slurry coating (2) overlaying the first coating (1), wherein both coatings (1, 2) have a chemical composition with a similar thermal expansion coefficient, and wherein the second coating (2) is very dense with a porosity < 1%, fully cured, and completely sintered and wherein the second coating (2) does only cover locally the first coating (1), so that said coating system (4) comprises a reduced roughness (Ra') with respect to the roughness (Ra) of the originally applied first coating (1).

10. Coating system (4) according to claim 8 or claim 9, **characterized in that** it is applied onto the surface of a gas turbine component (3) made of a Ni-, Co-, Fe-based superalloy or combinations thereof, that the first coating (1) is a ceramic thermal barrier coating, preferably made of chemically stabilized zirconia and that the second coating (2) is made by applying of a zirconia based slurry.

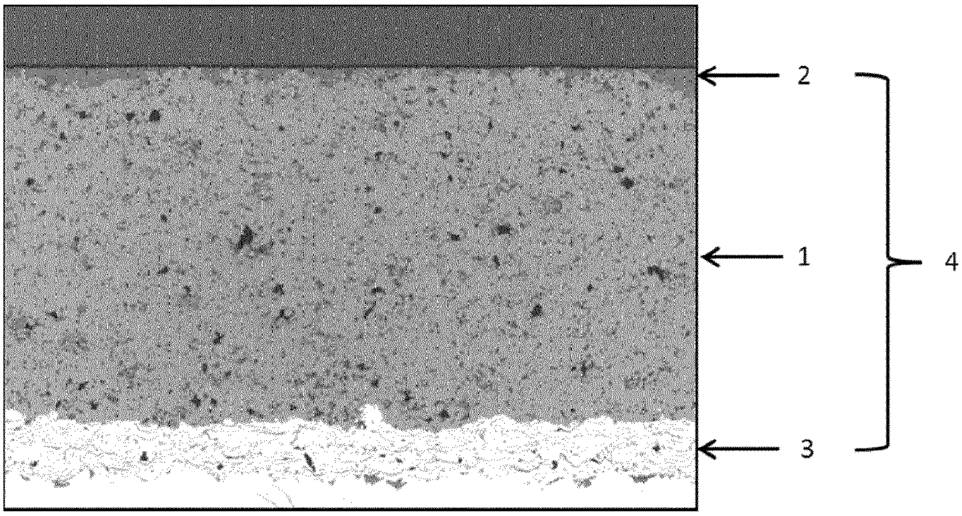

Fig. 1

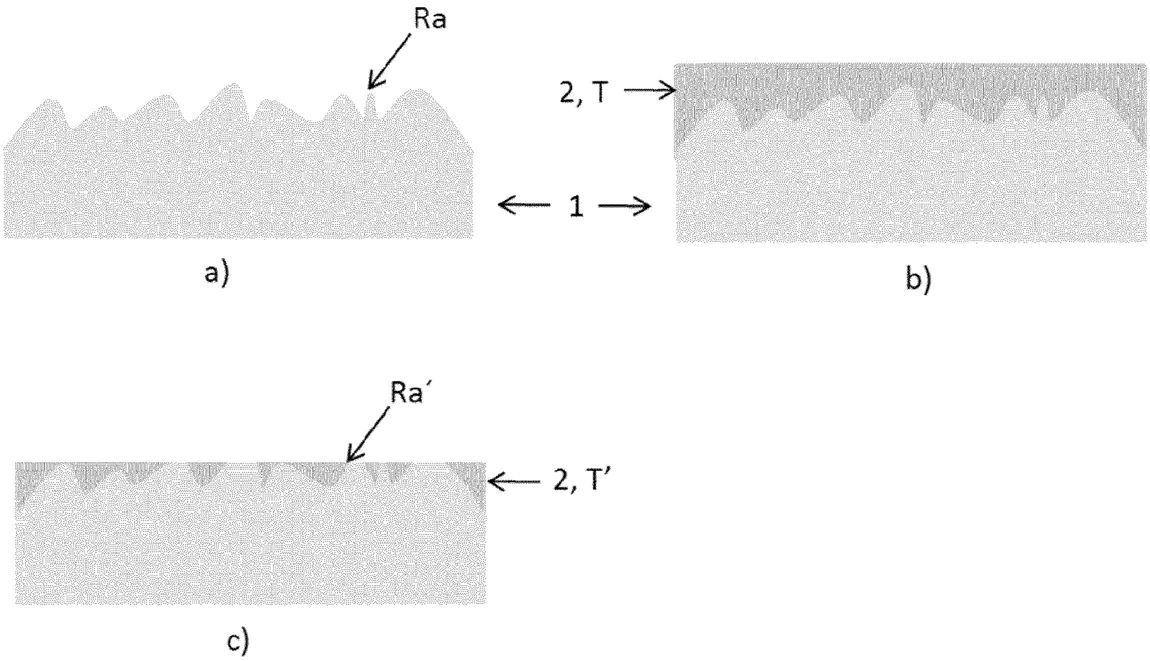

Fig. 2

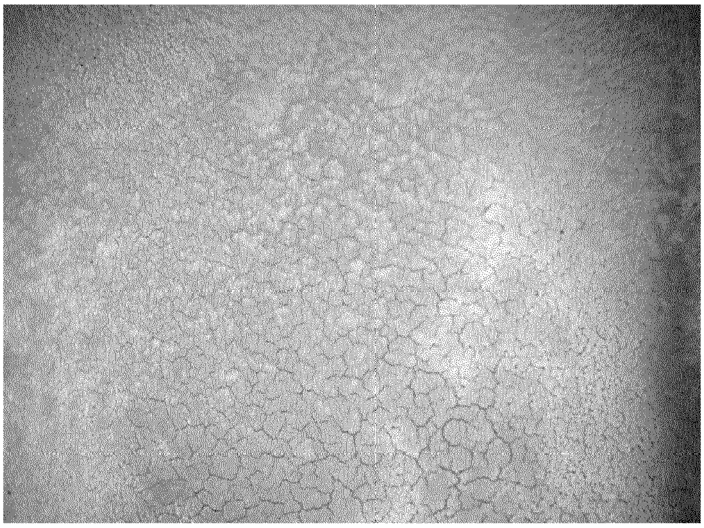

Fig. 3

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 14 17 8573

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	EP 1 088 908 A2 (GEN ELECTRIC [US]) 4 April 2001 (2001-04-04) * paragraphs [0014] - [0017], [0026] - [0027], [0047] - [0048], [0052], [0054] - [0058], [0078] - [0086], [0103]; claims 1-10 *	1-10	INV. C23C24/08 C23C28/04 C04B41/00
A	EP 2 287 129 A2 (GEN ELECTRIC [US]) 23 February 2011 (2011-02-23) * claims 1-8 *	1,5,6, 8-10	
A,D	EP 2 236 650 A1 (ROLLS ROYCE CORP [US]) 6 October 2010 (2010-10-06) * paragraphs [0005], [0007] - [0009], [0028] - [0036]; claims 1-16 *	1,3-10	
A	WO 2009/030049 A1 (ALCAN INT LTD [CA]; LEMIEUX ALAIN [CA]; LANGLAIS JOSEPH [CA]) 12 March 2009 (2009-03-12) * page 5, line 1 - page 11, line 4; claims 1-38; figure 1 *	1-10	

TECHNICAL FIELDS SEARCHED (IPC)
C23C
C04B

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	16 January 2015	Ruiz Martinez, Maria

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EP 14 17 8573

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16-01-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1088908 A2	04-04-2001	EP 1088908 A2	04-04-2001
		JP 2001226759 A	21-08-2001
		KR 20010050755 A	15-06-2001
		KR 20070104495 A	26-10-2007
		US 6294261 B1	25-09-2001
EP 2287129 A2	23-02-2011	EP 2287129 A2	23-02-2011
		JP 2011032163 A	17-02-2011
		US 2011229632 A1	22-09-2011
EP 2236650 A1	06-10-2010	EP 2236650 A1	06-10-2010
		US 2010255260 A1	07-10-2010
WO 2009030049 A1	12-03-2009	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 7368164 B2 **[0009]**
- US 20070099013 A1 **[0010]**
- US 6294261 B1 **[0011]**
- EP 1088908 A2 **[0011]**
- EP 2236650 A1 **[0011]**