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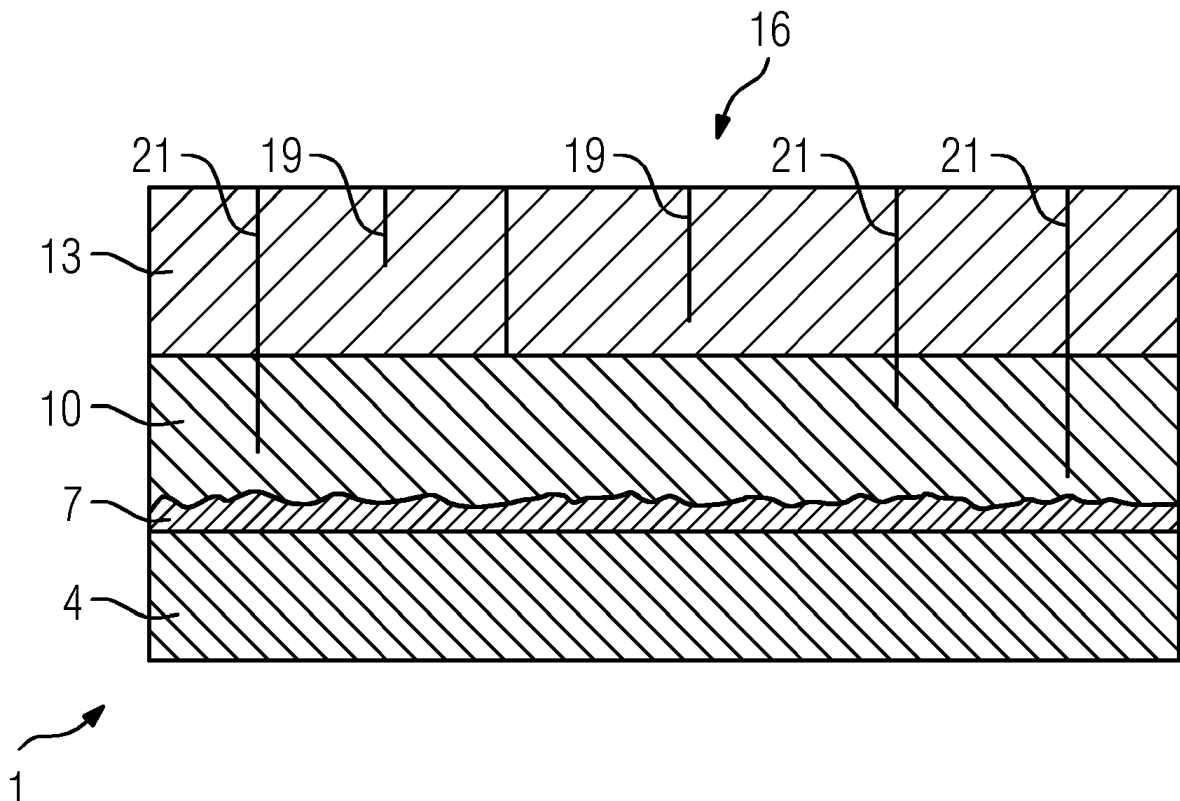
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(54) **DVC-COATING WITH FULLY AND PARTIALLY STABILIZED ZIRCONIA**

(57) A dense vertical cracked microstructure in a ceramic layer system made of an underline partially stabilized zirconia layer and an above laying fully stabilized zirconia layer show good erosion resistance and long life time.



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Description

[0001] The invention relates to a ceramic layer-system with partially and fully stabilized zirconia which has also a dense vertical cracked microstructure (DVC).

[0002] Field feedback has shown that the current Thermal Barrier Coatings (TBC) of turbines suffer from issues related to:

1) Erosion: turbine blades with high porosity coatings containing a large number of unmolten or semimolten particles show low erosion resistance.

The development during the last years has pushed thermal spray coatings porosity upwards. However, that has caused the shrinkage of the spray ability window that allows coatings to receive high porosity and good cohesion. As a result, erosion has started manifesting itself as a major issue for coatings in specific parts and engines.

2) Drilling damage: High porosity coatings contain less intimate contacts between splats or splat and substrate and thus the required energy for a crack to propagate is relatively low.

This problem has been addressed by drilling before the coating deposition and reopening of the holes after coating deposition. This approach minimizes the interaction between coating and laser and that reduces significantly the coating delamination around the drilled holes. However, since each part has to be processed twice, this solution is associated with longer drilling times that are reflected as increased cost.

3) Coating life: Thermal Spray porous coatings do not demonstrate at the same level the high strain tolerance along the coating thickness which can be seen in other coating types such as EB-PVD.

The thermal barrier coatings porosity has been increased to improve strain tolerance. However as mentioned above, that can reduce the spray ability process window and influence negatively the cohesion and erosion resistance of the coatings.

4) YSZ for TBC chemistries are currently limited to 1528K maximum temperature due to phase transformation issues.

New chemistries have been adopted that present phase stability in higher temperatures. However they show significantly lower fracture toughness compared to the partially stabilized zirconia and it is certain that their erosion resistance will be even less.

[0003] The task of the invention is therefore to solve the problems given above.

[0004] The problem is solved by a ceramic layer system according to claim 1.

[0005] In the subclaims further advantages are given

which can be abitrality combined with each other to yield additional advantages.

[0006] The figure and the description show only examples of the invention.

[0007] The problems named under point 1 are addressed by adopting Dense Vertical Cracked (DVC) coatings.

1) Erosion. DVC thermal barrier coatings have shown significantly lower rates compared to their porous counterparts. That means for the same chemistry a porous coating will show more than 3x the erosion rate compared to the DVC one.

2) DVC coatings have increased cohesion and adhesion compared to the typical porous coatings. The reason is that a very high ratio of fully molten particles deposit on hot substrate or hot previously deposited splats which promotes a good intimate bonding to develop between them. Improved adhesion requires high energy for a horizontal crack to propagate so that guarantees a lower delamination.

3) Coating life. Due to the intimate contact between splats, the DVC coatings show high fracture toughness along the parallel to the substrate plane. That, combined with their ability to accommodate thermal strain along the coating thickness due to their columnar microstructure ensures a high TBC life.

4) DVC microstructures can be adopted on the new coating chemistries. That will create a bilayer DVC with partially stabilized zirconia as a lower layer and fully stabilized zirconia as the upper layer. The lower layer will accommodate CTE mismatch with the bond coat and the TGO while the upper layer will provide the higher temperature capability.

[0008] The system consists of partially stabilized zirconia, especially 8YSZ as the high fracture toughness lower layer to accommodate the CTE mismatch with bond coat and TGO and a lower toughness upper layer of fully stabilized zirconia, especially 48YSZ to provide the high temperature capability. Unlike other possible bilayer coating approaches, the similar chemistry between the two coatings enhances their bonding.

[0009] Appropriate preheating of the DVC PSZ will prepare its surface to receive the fully molten particles of FSZ and due to the high local temperatures during spraying allow diffusion between the two similar materials. Ideally a number of the vertical cracks will progress from one coating to the other demonstrating the continuity between the two coatings. In this manner the interface which has shown to be the weakest link in other bi-layer systems will be reinforced.

[0010] The advantages that arise are:

1) The low fracture toughness of the FSZ with the

adoption of a DVC microstructure will significantly increase. That will improve the erosion resistance of the coating.

2) A good bonding between the two layers and as well with the bond coat will increase the drilling damage tolerance. Less delamination will be observed compared to other bilayer coating systems which have suffered in the past from drilling.

3) The columnar microstructure along the bilayer coating thickness will allow improved strain tolerance, thus increased coating life.

4) Higher temperature capability compared to single layer DVC coatings.

[0011] The figure shows a layer system 1.

[0012] The layer system 1 comprises a substrate 4 which is preferably metallic and very preferably made of a nickel or cobalt based super alloy.

[0013] On the substrate 4 a bond coat especially a metallic bond coat 7 and very especially a NiCoCrAlY-based bond coat 7 is applied on.

[0014] On this bond coat 7 there is a thermally grown oxide (TGO, not shown) layer which is formed during further application of the ceramic layers or by an additional oxidation step or at least during use of the layer system 1.

[0015] On the bond coat 7 there is applied a first zirconia layer 10 made of a Yttria partially stabilized zirconia.

[0016] The thickness of the partially stabilized zirconia layer 10 is preferable between 75um - 800um.

[0017] The porosity of the partially stabilized zirconia 10 is preferably lower than 5% and very preferably lower than 3%.

[0018] As an outer ceramic layer there is applied a fully stabilized zirconia layer 13, which is especially the outer most layer of the layer system 1.

[0019] The porosity of the fully stabilized zirconia 13 is lower than 5% and preferably lower than 3%.

[0020] The thickness of the fully stabilized zirconia 13 is between 50um - 800um.

[0021] The same parameters for thickness and porosity are also valid for the pyrochlore layer or pyrochlore/FSZ layer.

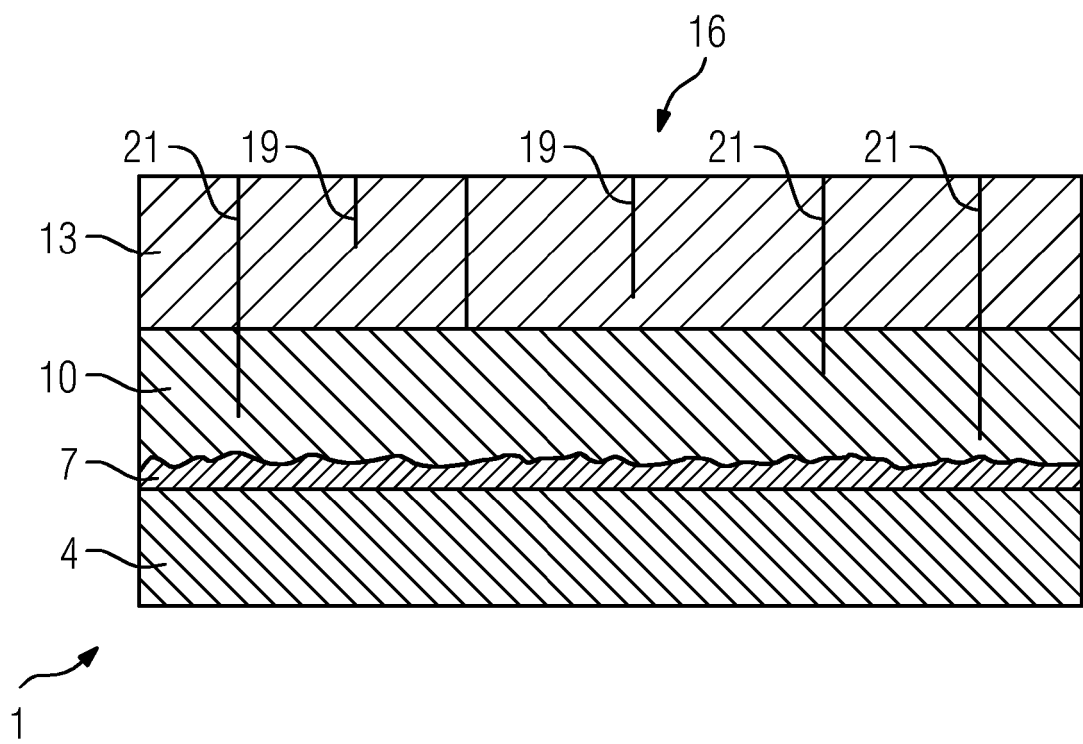
[0022] The stabilization in this zirconia based system can be reached by yttria or by any other rare earth element as known by the state of the art or by a combination of that.

[0023] Preferably yttrium is used for stabilization.

[0024] In this layers 10, 13 there are cracks 16 present, which 19 are mostly present in the outer most layer 13 and preferably some of them 21 are present in both layers 10, 13.

Claims

1. Ceramic layer system,
at least comprising:
 - a metallic substrate (4),
 - a metallic bond coat (7) on the substrate (4),
 - an inner partially stabilized zirconia layer (10) and
 - on it (10) a fully stabilized zirconia layer (13), wherein vertical cracks (16, 19, 21) are present, wherein cracks (19) are mostly present in the outer most layer 13, wherein the cracks (21) are present in both ceramic layers (10, 13), wherein the porosity of the fully stabilized zirconia layer (13) is lower than 50, which is dense vertically cracked, wherein the porosity of the partially stabilized zirconia layer is lower than 50, which is dense vertically cracked.
2. Ceramic layer system according to any of the preceding claims,
wherein the thickness of the partially stabilized zirconia layer (10) is between 75um - 800um.
3. Ceramic layer system according to any of the preceding claims,
wherein the thickness of the fully stabilized zirconia layer (13) is between 50um - 800um.
4. Ceramic layer system according to any of the preceding claims,
wherein the zirconia or the zirconia layers (10, 13) are stabilized by yttria.
5. Ceramic layer system according to any of the preceding claims,
wherein the partially stabilized zirconia is stabilized by yttria.





EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	US 2005/170200 A1 (NAGARAJ BANGALORE A [US] ET AL) 4 August 2005 (2005-08-04) * page 1, paragraph 7 * * page 2, paragraphs 15 - 17, 19 * * page 3, paragraph 21 * * figure 1 *	1-5	INV. C23C28/00 F01D5/28
Y	EP 1 908 856 A2 (UNITED TECHNOLOGIES CORP [US]) 9 April 2008 (2008-04-09) * page 2, paragraphs 1,2,6-8 * * page 3, paragraphs 13-15,17 * * page 4, paragraphs 21-23,26 * * page 5, paragraphs 28,29 * * figure 2B *	1-5	
A	EP 1 674 663 A2 (MITSUBISHI HEAVY IND LTD [JP]; UNIV TSINGHUA [CN]) 28 June 2006 (2006-06-28) * paragraph [0007] * * page 2, paragraphs 10, 14 * * page 6, paragraph 51 - page 8, paragraph 77 * * page 9, paragraph 89 * * page 12, paragraphs 112,113 * * page 14; table 1 * * figure 5 *	1-5	TECHNICAL FIELDS SEARCHED (IPC) C23C F01D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 25 September 2024	Examiner Joffreau, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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Application Number

EP 24 18 8396

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	KARGER M ET AL: "Atmospheric plasma sprayed thermal barrier coatings with high segmentation crack densities: Spraying process, microstructure and thermal cycling behavior", SURFACE AND COATINGS TECHNOLOGY, ELSEVIER, NL, vol. 206, no. 1, 18 June 2011 (2011-06-18), pages 16-23, XP028261462, ISSN: 0257-8972, DOI: 10.1016/J.SURFCOAT.2011.06.032 [retrieved on 2011-06-25] * the whole document *	1-5	
A	CANAN U. HARDWICKE ET AL: "Advances in Thermal Spray Coatings for Gas Turbines and Energy Generation: A Review", JOURNAL OF THERMAL SPRAY TECHNOLOGY., vol. 22, no. 5, 28 February 2013 (2013-02-28), pages 564-576, XP055221532, US ISSN: 1059-9630, DOI: 10.1007/s11666-013-9904-0 * page 567, paragraph 3.1; figure 5b *	1-5	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
Place of search Munich		Date of completion of the search 25 September 2024	Examiner Joffreau, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

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ON EUROPEAN PATENT APPLICATION NO.

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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10	Patent document cited in search report		Publication date	Patent family member(s)	Publication date
	US 2005170200	A1	04-08-2005	NONE	

15	EP 1908856	A2	09-04-2008	EP 1908856 A2	09-04-2008
				JP 2008095193 A	24-04-2008
				SG 141324 A1	28-04-2008
				US 2010098923 A1	22-04-2010
				US 2010196663 A1	05-08-2010

20	EP 1674663	A2	28-06-2006	CA 2529781 A1	14-06-2006
				EP 1674663 A2	28-06-2006
				EP 1959099 A2	20-08-2008
				US 2006151856 A1	13-07-2006

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