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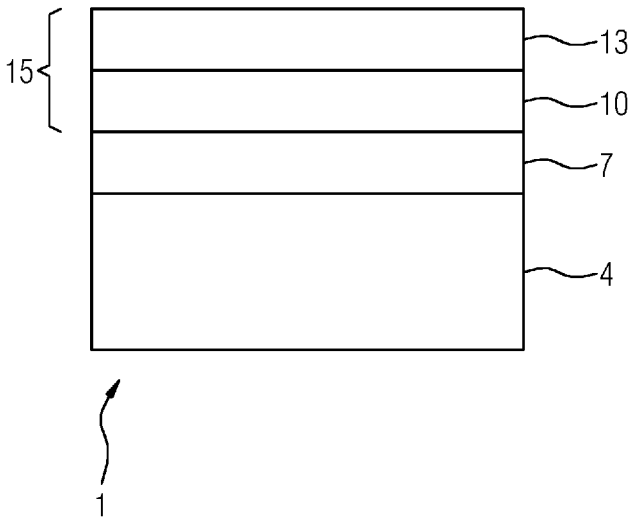
(54) **Title:** TWO-LAYER CERAMIC COATING SYSTEM



(57) **Abstract:** The invention relates to a layer system (1) comprising at least (in % by weight): a metallic substrate (4), optionally a metallic bonding layer (7) on the substrate (4) and a ceramic bottom layer (10) of partially stabilized, tetragonal zirconium oxide, with ytterbium oxide as stabilizer and a ceramic top layer (13) of fully stabilized cubic zirconium oxide on the ceramic bottom layer (10) wherein the proportion of stabilizers is between 17.5% and 25.5%.

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Two-layer ceramic coating system

The invention relates to a two-layer ceramic coating system.

Ceramics generally exhibit high temperature stability and are therefore often used as ceramic coatings on high-temperature components, such as in turbines, in particular in gas turbines.

Important in this type of application is the use of the ceramic as a coating on a substrate, which is often a metallic substrate.

Metallic bonding layers on the substrate, such as those based on NiCoCrAlY, but also ceramic bonding layers or TGO are known.

A two-layer coating system consisting of two ceramic layers is also often used.

Fully stabilized ceramic zirconium oxide layers with 20YSZ are state of the art, but need to be improved in terms of bonding to a ceramic sublayer.

The aim is therefore to improve the thermal insulation properties and service life of two layer-ceramic layer system.

It is therefore the task of the invention to solve the above-mentioned problem.

The problem is solved by a layer system according to claim 1

Ceramic layers based on zirconium oxide with stabilizers are known, whereby fully stabilized zirconium oxide is often used here due to its better thermal stability.

However, the aim of the idea is to use fully stabilized zirconium oxide with improved, in particular thermal stability, as well as good adhesion to a ceramic sublayer.

The figure schematically shows an example of the invention.

The figure and the description are only examples of the invention.

In a layer system 1, a ceramic layer 10 is applied to a metallic substrate, preferably using nickel- or cobalt-based superalloys as substrate 4, a metallic bonding layer 7 is present, which forms aluminum oxide (TGO, not shown).

The metallic bonding layer 7 is preferably also an aluminide, platinum aluminide or a NiCoCrAlY-X alloy as a base, optionally with x = Ta, Re, Fe and/or Si.

A ceramic top layer 13 can be applied by EB-PVD, plasma spraying (APS, ...), HVOF ... and preferably has a columnar structure or a segmented structure (DVC).

Preferably the porosity of the ceramic top layer 13 is lower than 10%.

The ceramic top layer 13 preferably has a layer thickness of 100µm to 1000µm.

A ceramic lower layer 10 is also present, but its layer thickness is at least 20% thinner than that of the ceramic top layer 13, which together with the ceramic top layer 13 form the ceramic layer system.
A ceramic lower layer 10 can be applied by EB-PVD, plasma spraying (APS, ...), HVOF ... .
Preferably the porosity of the ceramic lower layer 10 is lower than 10% or not higher than the porosity of the top layer 13.

All the following amounts are given in % by weight.

The ceramic bottom layer 10 comprises tetragonal zirconium oxide with ytterbium oxide as a stabilizer.
The following amounts are used:
11.5% to 13.5% ytterbium oxide.
Particularly preferably, 12.5% ytterbium oxide is used.
Equally preferably, only ytterbium oxide is used as a stabilizer. Some minor oxide impurities may be present.

A ceramic top layer 13 with a cubic structure of zirconium oxide (FSZ) is applied to the ceramic bottom layer 10.

The cubic zirconium oxide preferably has a yttrium oxide stabilized zirconium oxide (YSZ): the proportion of yttrium oxide being 18.0% to 22.0%, in particular 20.0%.
Preferably, only yttrium oxide is used as a stabilizer. Some minor oxide impurities may be present.

It is also possible to use cubic zirconium oxide with stabilizers of yttrium oxide, ytterbium oxide and gadolinium oxide:
Yttrium oxide represents the largest proportion in comparison to the other two stabilizers.
Preferably, only these stabilizers are used.
The following proportions are preferably used in each case:
9.0% - 11.0% yttrium oxide,
4.5% - 6.5% ytterbium oxide and
4.0% - 6.0% gadolinium oxide.
Particularly preferred are in each case
9.5% - 10.0% yttrium oxide,
5.2% - 6.0% ytterbium oxide and
4.8% - 5.6% gadolinium oxide.
Preferably, only these stabilizers yttrium oxide, ytterbium oxide and gadolinium oxide are used. Some minor oxide impurities may be present.

The fully stabilized zirconium oxide (FSZ) is preferably also stabilized with 14.0% to 16.0% ytterbium oxide (Yb_2O_3) in particular with 14.5% to 15.5% ytterbium oxide (Yb_2O_3) and stabilized with 4.0% to 6.0% yttrium oxide (Y_2O_3) and
optionally hafnium oxide and/or aluminum oxide.
The ceramic material preferably comprises 4.5% to 5.5% yttrium oxide (Y_2O_3).
The ceramic material preferably optionally comprises:
Hafnium oxide (HfO_2) with 0.2% to 4.0%,
in particular 0.5% to 2.5% hafnium oxide (HfO_2).

Example for underlayer 10:
12.4% Yb_2O_3 - ZrO_2
examples for top layer 13 in combination with the example above:
20.1% Y_2O_3 - ZrO_2
or
15.0% Yb_2O_3 / 4.9% Y_2O_3 - ZrO_2
or
10.0% Y_2O_3 / 5.5% Yb_2O_3 / 5.3% Gd_2O_3 - ZrO_2
for which good properties were achieved.

1. Layer system (1)
comprising at least (in % by weight)
a metallic substrate (4),
optionally a metallic bonding layer (7) on the substrate (4) and
a ceramic underlayer (10)
of partially stabilized, tetragonal zirconium oxide,
with ytterbium oxide as stabilizer,
preferably 11.5% - 13.5% ytterbium oxide,
particularly preferably 12.5% ytterbium oxide,
and a ceramic top layer (13)
of fully stabilized cubic zirconium oxide on the ceramic bottom layer (10),
wherein the proportion of stabilizers of the ceramic top layer (13) is between 17.5% and 26.0%.

2. Layer system according to claim 1,
in which only ytterbium oxide is used as a stabilizer
for the ceramic sublayer (10).

3. Layer system according to one or both of claims 1 or 2,
in which the ceramic top layer (13) comprises (in % by weight) yttrium oxide stabilized zirconium oxide,
wherein the proportion of yttrium oxide is 18.0 wt.% to 22.0 wt.%,
in particular 20.0% by weight,
in particular only yttrium oxide is used.

4. Layer system according to one or both of claims 1 or 2,
in which the ceramic top layer (13) comprises (in % by weight) zirconium oxide,
wherein stabilizers of yttrium oxide, ytterbium oxide and gadolinium oxide are present,
wherein preferably the following proportions are given:
9.0% - 11.0% yttrium oxide,
4.5% - 6.5% ytterbium oxide and
4.0% - 6.0% gadolinium oxide,

preferably 9.75% - 10.0% yttrium oxide,
preferably 5.2% to 6.0% ytterbium oxide and
preferably 4.8% - 5.6% gadolinium oxide
are present in each case,
in particular only these three stabilizers yttrium oxide, ytterbium oxide and gadolinium oxide are used.

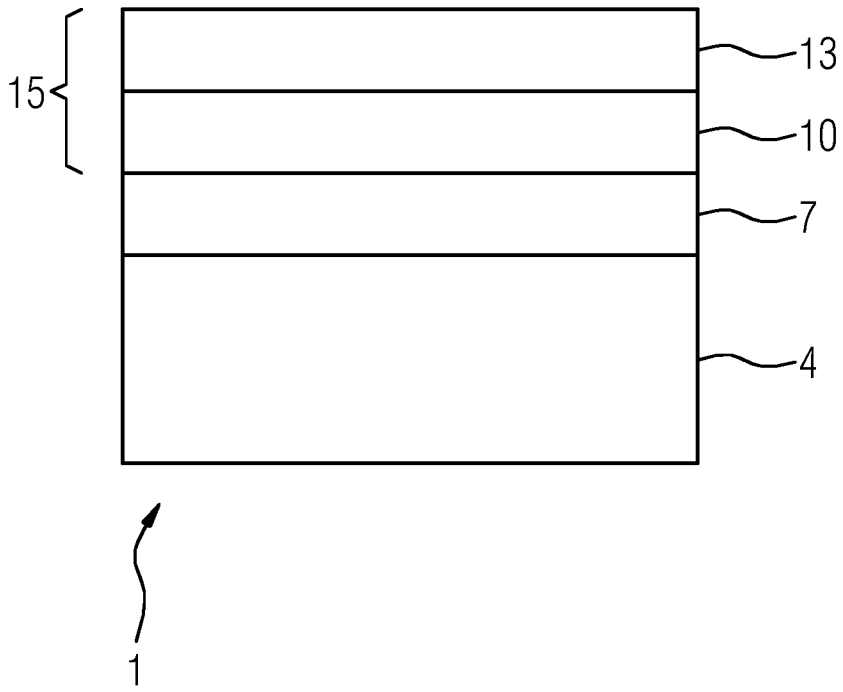
5. Layer system according to one or both of claims 1 or 2, wherein the ceramic top layer (13) comprises zirconium oxide,
wherein stabilizers (in % by weight) of yttrium oxide and ytterbium oxide are present,
wherein preferably the following proportions are given:
ytterbium oxide (Yb_2O_3) with 14.0% to 16.0%,
in particular with 14.5% to 15.5% ytterbium oxide
as well as
with 4.0% to 6.0% yttrium oxide and optionally hafnium oxide and/or aluminum oxide.

6. Layer system according to claim 5,
in which the ceramic top layer (13) comprises zirconium oxide (in % by weight),
wherein stabilizers of yttrium oxide and ytterbium oxide are present,
wherein the following proportions are given:
15% ytterbium oxide,
4.5% to 5.5% yttrium oxide,
optionally
hafnium oxide with 0.2% to 4.0%,
in particular 0.5% to 2.5% hafnium oxide.

7. Layer system according to one or more of claims 1, 2, 3, 4, 5 or 6,
comprising
a metallic adhesion promoter layer (7) between the ceramic underlayer (10) and the metallic substrate (4),
in particular directly on the substrate (4),
wherein the adhesion promoter layer (7) comprises an

alloy of the type NiCoCrAlY-X,
X is optionally and selected from the group: Ta, Re and/or Si,
in particular NiCoCrAlY or NiCoCrAlY-Ta.

8. Layer system according to one or more of the claims 1, 2, 3, 4, 5, 6 or 7,
in which the ceramic sublayer (10) under the ceramic layer (13) is at least 20% thinner.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INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER

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ADD.

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 C04B

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 practicable, 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.
X	US 6 887 595 B1 (DAROLIA RAMGOPAL [US] ET AL) 3 May 2005 (2005-05-03) claims 1-16 column 2, line 48 - column 3, line 51 column 8, line 18 - column 9, line 19	1-8
A	WO 2022/174996 A1 (FLORES RENTERIA ARTURO [DE]) 25 August 2022 (2022-08-25) claims 1-20 page 1, line 27 - page 3, line 31	1-8
A	US 2022/041510 A1 (SIEMENS AG [DE]) 10 February 2022 (2022-02-10) claims 1-17 paragraphs [0009] - [0016] paragraphs [0036], [0038] - [0039]	1-8

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

☒ See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2024	22/10/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP2024/074873

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