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(54) ARTICLE COMPRISING A BOND LAYER AND A COATING LAYER

(57) The present invention concerns an article comprising: (i) at least one substrate selected from the group consisting of Pt substrate, Pt/Rh alloy substrate, superalloys substrates, iron alloys substrates, metal carbide substrates, boron carbide substrates, boron nitride substrate, silicon nitride substrates, metal oxides substrates and combinations thereof, said substrate having at least one surface; and (ii) one bond layer at least partially covering said surface of said substrate; said bond layer comprising yttria-stabilized zirconia, or titanium oxide, or chromium oxide; and (iii) at least one layer (L1) at least partially covering said bonding layer; said layer (L1) comprising silicon carbide. The article shows good heat stability.

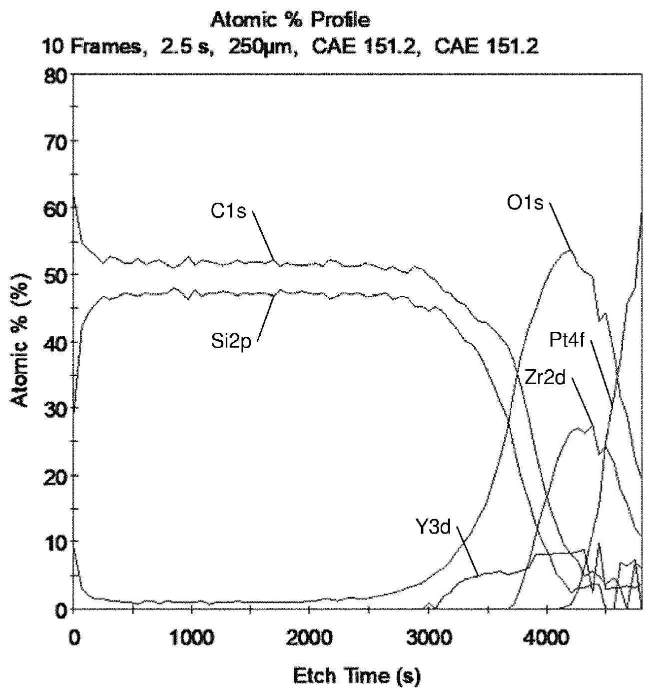


Fig. 1

EP 4 450 762 A1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to the field the field of thermal barrier coatings.

STATE OF THE ART

[0002] Certain metals form volatile oxides when heated at high temperature (for example above 1000°C) in presence of oxygen. This is for example the case of nickel (Ni), tungsten (W), rhodium (Rh), platinum (Pt), ruthenium (Ru), and alloys thereof. The same phenomenon may also happen with other alloys such as alloys of W, Cr, Y and Stainless steel.

[0003] Unfortunately, the aforementioned metals and alloys are often comprised in articles such as devices and tools which are used at high temperature in presence of oxygen. In these conditions, the aforementioned metals form oxides which undergo sublimation. The sublimation of the aforementioned oxides usually results in a significant mass loss for the articles that comprise them.

[0004] That is for example the case of crucibles and bushings which are made of a platinum alloy and are used in glass industry that are in contact with molten glass at a temperature which can reach 1400 °C. At these temperatures, oxides will form in the presence of oxygen. These oxides are volatile and will undergo sublimation above 1000 °C which will result in a significant mass loss for the components during glass production.

[0005] Therefore, there is a need to provide heat stability at high temperature in presence of oxygen to articles comprising the aforementioned metals.

[0006] CN 101967313 B is concerned with the same problem and discloses a coating comprising 20 - 50 wt.% of silicon oxide 20-45 wt.% of alumina, 5-15 wt.% of sodium silicate, 10-25 wt.% of sodium tetraborate. The application of the coating requires a step of mixing these components with water and a phenolic resin followed by a heating step to about 80 °C - 120 °C.

[0007] CN 102442830 B discloses a coating powder for high-temperature leak-proof plate which consists of 25-55 wt.% of SiO_2, 35-70 wt.% of Al_2O_3, 1-9 wt.% of MgO, 0-1.2 wt.% of CeO_2, 0-0.2 wt.% of Li_2O and: 0-0.2 wt.% Bi_2O_3.

[0008] These solutions are complex to carry out because they require many different steps, manipulating powders, mixing many different compounds together in water. Sometimes they even require the use of a phenolic resin. This complexity increases the risk of errors and/or accidents for the user/operator who is trying to prepare such coatings.

[0009] Moreover, coatings comprising many different elements that are difficult to recycle. Furthermore, they can contain elements that may form alloys with the metals contained in the substrate which render recycling even more difficult.

[0010] There is thus a continuous need to provide articles with good heat stability. The solution to this problem must not require the preparation of solutions or the use of organic resins and must be easily applicable, in particular through physical vapor deposition techniques (PVD).

INVENTION SUMMARY

[0011] The inventors have surprisingly found that the present invention can solve the above identified problems.

[0012] The present invention concerns an article comprising:

(i) at least one substrate selected from the group consisting of Pt/Rh alloy substrates, Pt substrates, superalloys substrates, iron alloys substrates, metal carbide substrates, boron carbide substrates, boron nitride substrate, silicon nitride substrates, metal oxides substrate and combinations thereof, and having at least one surface; and
(ii) one bond layer at least partially covering said surface of said substrate; said bond layer comprising yttria-stabilized zirconia, or titanium oxide, or chromium oxide; and
(iii) at least one layer (L1) at least partially covering said bonding layer; said layer (L1) comprising silicon carbide.

The inventors have surprisingly found that the articles according to the present invention can be applied by PVD techniques and have good heat stability do not require the preparation of solutions or the use of organic resins.

DETAILED DESCRIPTION

[0013] In the context of the present invention, the term "comprising" should not be interpreted as excluding features or elements other than those explicitly mentioned. It should be construed as specifying the presence of the features or elements indicated, but does not exclude the presence or addition of one or more other features or elements. Thus, the scope of the expression "a method comprising steps A and B" should not be limited to methods consisting only of steps A and B. Similarly, a composition comprising components A and B should not be limited to compositions consisting only of components A and B. Accordingly, the terms "comprising" and "including" encompass the terms more restrictive "consisting essentially of" and "consisting of".

[0014] In the context of the present invention, if an element or component is said to be selected from a list of recited elements or components, it should be understood that the element or component can also be any one of the individual recited elements or components in said list, or can also be selected from a group consisting of any two or more of the explicitly listed elements or components.

The article

[0015] Said article according to the present invention may be any article without any restriction of shape. Preferably, said article is an article obtainable by a physical vapor deposition process (PVD). Examples of suitable articles include but are not limited to: tools, , aircraft components, particularly aircraft components intended to be subjected to high temperature, bushings used for glass fibers production, vessels and tanks, particularly vessels and tanks intended to be subjected to corrosive media at high temperature.

[0016] Preferably, said article must be suitable for use at a temperature of at least 800°C, more preferably at least 1000°C, even more preferably at least 1200°C. Preferably, said article must be suitable for use at a temperature of at most 1600°C, more preferably at most 1500°C, even more preferably at least 1450°C.

[0017] Within the context of the present invention, an article is suitable for use at the above temperatures, if it is able to function at the above temperatures. For example, an article is not suitable for use at the above temperature if components in said article are able to melt at the above temperatures. In particular, that means that said article is suitable for use at the above temperature even if it is in contact with a fluid, matter or an object which is at the above temperature.

[0018] Preferably, said article is suitable for use in contact with a fluid, or a material such as hot air or molten glass at a temperature of at least at least 800°C, more preferably at least 1000°C, even more preferably at least 1200°C. Preferably, said article is suitable for use in contact with a fluid such as molten glass at a temperature of at most 1600°C, more preferably at most 1500°C, even more preferably at most 1450°C.

The substrate

[0019] Said article according to the present invention comprises at least one substrate. Said substrate is selected from the group consisting of Pt substrates, Pt/Rh alloy substrates, superalloys substrates, iron alloys substrates, metal carbide substrates, boron carbide substrates, boron nitride substrate, silicon nitride substrates, metal oxides substrate and combinations thereof.

[0020] Within the context of the present invention, the term "substrate" is given its normal meaning in the field of thermal barrier coating. Any suitable substrate may be used. Particularly, said substrate is suitable for use in PVD coating techniques. Examples of suitable substrates include but are not limited to tools, , aircraft components, particularly aircraft components intended to be subjected to high temperature (above 1000°C), bushings used for glass fibers production, vessels and tanks, particularly vessels and tanks intended to be subjected to corrosive media at high temperature (above 1000°C). The substrate may also be a piece or a layer or a part which is incorporated in another object such as for example (but being limited to): tools, aircraft components, particularly aircraft components intended to be subjected to high temperature (above 1000°C), bushings used for glass fibers production, vessels and tanks, particularly vessels and tanks intended to be subjected to corrosive media at high temperature (above 1000°C).

[0021] The term "Pt substrate" is given its normal meaning in the field. Generally, a Pt substrate comprises over 99 wt.% of a Pt. The remaining wt.% may for example be impurities. Preferably, a Pt substrate consists of Pt.

[0022] The term "Pt/Rh alloy substrate" is given its normal meaning in the field. Generally, a Pt/Rh alloy substrate comprises over 99 wt.% of a Pt/Rh alloy. The remaining wt.% may for example be impurities.

[0023] Preferably, a Pt/Rh alloy substrate consists of at least one Pt/Rh alloy substrate. Said Pt/Rh alloy substrate may preferably comprise at least 0 at. % of Rh, preferably at least 5 at. % of Rh, more preferably at least 10 at. % of Rh. It is understood that said Pt/Rh alloy substrate may comprise at most 30 at. % of Rh, more preferably at most 20 at. % of Rh or at most 15 at. % of Rh, based on the total atoms of Pt and Rh in said Pt/Rh alloy substrate. Said Pt/Rh alloy substrate may preferably comprise at least 70 at. % of Pt, preferably at least 75 at. % of Pt, more preferably at least 80 at. % of Pt. It is understood that said Pt/Rh alloy substrate may comprise at most 100 at. % of Pt, more preferably at most 95 at. % of Pt or at most 90 at. % of Pt, based on the total amount of atoms of Pt and Rh in said Pt/Rh alloy substrate. Preferably, said Pt/Rh substrate comprises 10 at. % of Rh and 90 at. % of Pt or 20 at. % of Rh and 80 at. % of Pt, based on the total amount of atoms of Pt and Rh in said Pt/Rh alloy substrate.

[0024] The term "superalloy substrate" is given its normal meaning in the field. Examples of superalloys substrates include but are not limited to: Ni based superalloys, Co based superalloys, Fe based superalloys. Generally, a superalloy substrate comprises over 99 wt.% of a superalloy. The remaining wt.% may for example be impurities. Preferably, a superalloy substrate consists of superalloy(s). Example of superalloy are Ni-based, Co-based or Cr-based austenitic alloys. Superalloy substrates may for example comprise between 50 and 70 wt.% of Ni and/or Fe and/or Co, and between 5 and 20 wt.% of Cr, and between 0.5 and 6 wt.% of Al, and between 1 and 4 wt.% of Ti, and between 0.05 and 0.2 wt.% of C, and between 0 and 0.1 wt.% of B and/or Zr, and between 0 and 5 wt.% of Nb, and between 1 and 10 wt.% of Re, W, Hf, Mo and/or Ta, based on the total weight of said superalloy substrate.

[0025] The term "metal carbide substrate" is given its normal meaning in the field. Generally, metal carbide substrate comprises over 99 wt.% of a metal carbide. Preferably, a metal carbide substrate consists of metal carbide. The remaining wt.% may for example be impurities. Example of metal carbide substrates include but are not limited to: tungsten carbide (WC).

[0026] The term "boron carbide substrate" is given its normal meaning in the field and may for example encompass B_4C substrates. Generally, a boron carbide substrate comprises over 99 wt.% of a boron carbide. The remaining wt.% may be impurities. Preferably, a boron carbide substrate consists of boron carbide.

[0027] The term "boron nitride" is given its normal meaning in the field and may for example encompass BN substrates. Generally, a boron nitride substrate comprises over 99 wt.% of boron nitride. The remaining wt.% may be impurities. Preferably, a boron nitride substrate consists of boron nitride.

[0028] The term "silicon nitride substrate" is given its normal meaning in the field and may for example encompass Si_3N_4 substrates. Generally, a silicon nitride substrate comprises over 99 wt.% of a silicon nitride. The remaining wt.% may be impurities. Preferably, a silicon nitride substrate consists of silicon nitride.

[0029] The term "metal oxide substrate" is given its normal meaning in the field. Generally, a metal oxide substrate comprises over 99 wt.% of a metal oxide or a mixture of metal oxides. The remaining wt.% may be impurities. Preferably, a metal oxide substrate consists of a metal oxide.

[0030] Example of metal oxide substrates include but are not limited to ZrO_2, Al_2O_3, SiO_2 and combination thereof.

[0031] The term "iron alloy substrate" is given its normal meaning in the field. Generally, an iron alloy substrate can comprise over 99 wt.% of iron alloy. The remaining wt.% can be impurities. Examples of suitable iron alloys include but are not limited to steel and stainless-steel alloys.

[0032] Preferably, said substrate may be selected from the group consisting of Pt substrate, Pt/Rh alloy substrate, superalloy substrate, WC substrate, B_4C substrate, Si_3N_4 substrate, ZrO_2 substrate, Al_2O_3 substrate and combinations thereof.

The bond layer

[0033] Said article according to the present invention comprises (ii) one bond layer covering at least partially said surface of said substrate and comprising yttria-stabilized zirconia (YSZ), or titanium oxide, or chromium oxide.

[0034] Preferably, the bond layer may directly cover the surface of said substrate. Within the context of the present invention "directly cover" is intended to denote that the bond layer is in direct contact with the surface of the substrate, in other words, in this case, the article does not comprise any other layer between the bond layer and the substrate.

[0035] Advantageously, the bond layer enables good adherence of the layer (L1) on the substrate.

[0036] Preferably, said bond layer comprises at least 90 wt.%, more preferably at least 95 wt.%, even more preferably at least 99 wt.%, even more preferably at least 99.9 wt.% of yttria-stabilized zirconia (YSZ), titanium oxide, or chromium oxide, based on the total weight of said bond layer. If desired, said bond layer consists of yttria-stabilized zirconia (YSZ), titanium oxide, or chromium oxide.

[0037] YSZ is known in the art as being a ceramic made of "zirconia" (ZrO_2) and "yttria" (Y_2O_3).

[0038] Preferably, said YSZ comprises at least 5 at. %, more preferably at least 7 at. %, even more preferably at least 8 at. % of yttrium. It is understood that said YSZ preferably comprises at most 15 at. %, more preferably at most 13 at. %, even more preferably at most 12 at. % of yttrium, based on the total amount of atoms in said YSZ.

[0039] Preferably, said YSZ comprises at least 20 at. %, more preferably at least 25 at. % of zirconium, based on the total amount of atoms in said YSZ. It is understood that said YSZ preferably comprises at most 40 at. % of zirconium, preferably at most 35 at. % of zirconium, based on the total amount of atoms in said YSZ.

[0040] Preferably, said YSZ comprises at least 50 at. % of oxygen, more preferably at least 55 at. % of oxygen, based on the total amount of atoms in said YSZ. It is understood that said YSZ may comprise at most 70 at. % of oxygen, more preferably at most 65 at. % of oxygen, based on the total amount of atoms in said YSZ.

[0041] Preferably, said YSZ comprises at least 3 mol. % and preferably at most 6 mol. % of yttria, based on the total moles of zirconia and yttria in said YSZ. Alternatively, said YSZ comprises 3 mol. % or 6 mol. % of yttria based on the total moles of zirconia and yttria in said YSZ.

[0042] Preferably, said YSZ has a t' phase, namely metastable tetragonal phase.

[0043] In a preferred embodiment, said bon layer comprises based on the total weight of said bond layer, at least 99 w.% of YSZ having at t' phase, wherein said YSZ comprises at least 3 mol. % and at most 6 mol. % of yttria, based on the total moles of zirconia and yttria in said YSZ.

[0044] Within the context of the present invention, "titanium oxide" does not only refer to TiO_2, but it also encompasses other titanium oxides. For example, the titanium atom(s) of the titanium oxides may have an oxidation state of II, III or IV. Said titanium oxide may also be a stoichiometric or non-stoichiometric oxide. Suitable titanium oxides include but are not limited to: TiO_2, $TiO_{1.7}$, $TiO_{1.9}$, TiO, Ti_2O_3, Ti_3O, Ti_2O, $TiO_{0.68}$, $TiO_{0.75}$, and mixtures thereof.

[0045] Preferably, said titanium oxide has the formula (I):

$$TiO_x \qquad \text{Formula (I)}$$

wherein x is a rational number and is at least 1 and at most 2, more preferably at least 1.7 and at most 2, even more preferably x is 1.7, 1.9 or 2.

[0046] In an embodiment, said bond layer comprises based on the total weight of said bond layer, at least 99 w.% of titanium oxide selected from the group consisting of TiO_2, $TiO_{1.7}$, $TiO_{1.9}$, TiO, Ti_2O_3, Ti_3O, Ti_2O, $TiO_{0.68}$, $TiO_{0.75}$, and mixtures thereof.

[0047] In an embodiment, said bon layer comprises based on the total weight of said bond layer, at least 99 w.% of titanium oxide having the formula (I), wherein x is at least 1.7 and at most 2.

[0048] Within the context of the present invention, "chromium oxide" does not only refer to CrO or Cr_2O_3, but it also encompasses other chromium oxides. For example, the chromium atom(s) of the chromium oxides may have an oxidation state of at least I and at most VI. Said chromium oxide may also be a stoichiometric or non-stoichiometric oxide. Suitable chromium oxides include but are not limited to: CrO, Cr_2O_5, Cr_2O_3, CrO_2, CrOs, CrOs, Cr_3O_8, Cr_8O_{21}, $Cr_2O_{2.8}$ and mixtures thereof.

[0049] Preferably, said chromium oxide has the formula (II):

$$Cr_yO_z \qquad \text{Formula (II)}$$

wherein y is an integer of at least 1 and at most 8 and z is a rational number of at least 1 and at most 21.

[0050] Preferably, y is an integer of at most 5, more preferably at most 3, even more preferably at most 2.

[0051] Preferably z is a rational number of at most 5, more preferably at most 3.

[0052] Preferably, if y is 1, z is a rational number of at least 1 and at most 5, more preferably at most 3, even more preferably at most 2.

[0053] Preferably, if y is 2, z is a rational number of at least 3 and at most 5, more preferably at most 3.

[0054] In a preferred embodiment, y is 1 or 2 and z is a rational of at least 1 and at most 5 with the proviso that if y is 1, z is a rational number of at least 1 and at most 5, more preferably at most 3, even more preferably at most 2 and if y is 2, z is a rational number of at least 3 and at most 5, more preferably at most 3.

[0055] In an embodiment, said bon layer comprises based on the total weight of said bond layer, at least 99 w.% of chromium oxide selected from the group consisting of CrO, Cr_2O_5, Cr_2O_3, CrO_2, CrOs, CrOs, Cr_3O_8, Cr_8O_{21}, $Cr_2O_{2.8}$ and mixtures thereof.

[0056] In an embodiment, said bond layer comprises based on the total weight of said bond layer, at least 99 w.% of chromium oxide having the formula (II) wherein y is y is 1 or 2 and z is a rational of at least 1 and at most 5 with the proviso that if y is 1, z is a rational number of at least 1 and at most 5, more preferably at most 3, even more preferably at most 2 and if y is 2, z is a rational number of at least 3 and at most 5, more preferably at most 3.

[0057] Preferably said at least one bond layer has a thickness of at least 100 nm, more preferably at least 150 nm, even more preferably at least 200 nm. It is understood that said at least one bond layer has a thickness of at most 1000 nm, more preferably at most 900 nm, even more preferably at most 800 nm.

[0058] In a preferred embodiment, said at least one bond layer has a thickness of at least 100 nm and at most 1000 nm, more preferably at least 150 nm and at most 900 nm, even more preferably at least 200 nm and at most 800 nm.

The layer (L1)

[0059] Said article according to the present invention further comprises at least one layer (L1) at least partially covering said bonding layer and comprising silicon carbide.

[0060] Said at least one layer (L1) may also cover totally said bonding layer.

[0061] Preferably, the layer (L1) may directly cover said bond layer. Within the context of the present invention "directly cover" is intended to denote that the layer (L1) is in direct contact with the bond layer, in other words, the article does not comprise any other layer between the bond layer and the layer (L1).

[0062] Within the context of the present invention, silicon carbide is given its normal meaning in the field.

[0063] Said silicon carbide may be stoichiometric or non-stoichiometric silicon carbide.

[0064] Preferably, said at least one layer (L1) comprises based on the total weight of said layer (L1), at least 50 wt.%, preferably at least 60 wt.%, more preferably at least 75 wt.%, even more preferably at least 80 wt.%, even more preferably at least 85 wt.%, even more preferably at least 90 wt.%, even more preferably at least 95 wt.%, even more preferably at least 99.9 wt.% of silicon carbide.

[0065] It is understood that said at least one layer (L1) preferably comprises based on the total weight of said layer (L1), at most 100 wt.% of silicon carbide.

[0066] If desired, said at least one layer (L1) consists of silicon carbide.

[0067] Preferably, in addition to the silicon carbide, said at least one layer (L1) comprises at least 1 at. %, more preferably at least 2 at. %, even more preferably at least 3 at. %, even more preferably at least 5 at. % of C. It is understood that said at least one layer (L1) may comprise at most 15 at. %, more preferably at most 12 at. %, even more preferably at most 10 at. % of C. In this case, the C is carbon which is to be considered as different and additional to the carbon forming the SiC.

[0068] Thus, said at least one layer (L1) comprises Si (silicon) and C (carbon). Preferably said at least one layer (L1) has a Si/C atomic ratio of at least 0.60, more preferably at least 0.7, even more preferably at least 0.8. It is understood that said at least one layer (L1) has a Si/C atomic ratio of at most 2.00, more preferably at most 1.60, even more preferably at most 1.10.

[0069] In a preferred embodiment, said at least one layer (L1) has a Si/C atomic ratio of at least 0.6 and at most 2.00, more preferably at least 0.7 and at most 1.60, even more preferably at least 0.8 and at most 1.1.

[0070] In the context of the present invention, the Si/C atomic ratio refers to the ratio of total at. % of Si over the total at. % of C, wherein the at. % of Si and C are based on the total atoms in said layer (L1).

[0071] In a preferred embodiment, said at least one layer (L1) comprises based on the total weight of said at least one layer (L1) at least 85 wt.% of SiC and at least 2 at.% and at most 15 at.% of C.

[0072] In a preferred embodiment, said substrate is a Pt/Rh alloy substrate, said bond layer comprises based on the total weight of said bond layer, at least 99 w.% of YSZ having at t' phase, wherein said YSZ comprises at least 3 mol.% and at most 6 mol.% of Yttria, based on the total moles of zirconia and yttria in said YSZ; said at least one layer (L1) comprises based on the total weight of said at least one layer (L1) at least 85 wt.% of SiC and additionally at least 2 at.% and at most 15 at.% of C; said bon layer directly covers said substrate and said layer (L1) directly covers said bond layer.

[0073] Said at least one layer (L1) may also comprise other materials such as for example TiB_2.

[0074] Preferably said at least one layer (L1) comprises based on the total weight of said layer (L1) at most 65 wt.% of TiB_2, more preferably at most 50 wt.%, even more preferably at most 30 wt.% of TiB_2.

[0075] If desired, said at least one layer (L1) may comprise at least 10 wt.% or 20 wt.% of TiB_2.

[0076] Preferably said at least one layer (L1) has a thickness of at least 100 nm, more preferably at least 150 nm, even more preferably at least 200 nm. It is understood that said at least one layer (L1) has a thickness of at most 20000 nm, more preferably at most 15000 nm, even more preferably at most 10000 nm.

[0077] In a preferred embodiment, said at least one layer (L1) has a thickness of at least 100 nm and at most 20000 nm, more preferably at least 150 nm and at most 15000 nm, even more preferably at least 200 nm and at most 10000 nm.

[0078] If desired, said article according to the present invention may comprise at least one additional layer (L2) at least partially or totally covering said layer (L1).

[0079] In a preferred embodiment, said at least one layer (L2) comprises based on the total weight of said layer (L2), at least 50 wt.%, preferably at least 60 wt.%, more preferably at least 75 wt.%, even more preferably at least 90 wt.%, even more preferably at least 99.9 wt.% of TiB_2.

[0080] It is understood that said at least one layer (L2) preferably comprises based on the total weight of said layer (L2), at most 100 wt.% of TiB_2.

[0081] If desired, said at least one layer (L2) consists of TiB_2.

[0082] Said at least one layer (L2) may also comprise other materials such as for example silicon carbide.

[0083] If desired, said article according to the present invention may comprise a plurality of layers (L1) and (L2).

[0084] In one embodiment, said article comprises a plurality of layers (L1) and (L2) wherein each layer (L1) is at least partially or totally covered by a layer (L2). In an alternative embodiment, said article comprises a plurality of layers (L1) and (L2) wherein each layer (L2) is at least partially or totally covered by a layer (L1).

[0085] If desired, at least one layer of SiO_2 may cover said layer (L1).

[0086] Preferably said at least one layer SiO_2 has a thickness of at least 10 nm, more preferably at least 20 nm, even more preferably at least 30 nm. It is understood that said at least one layer of SiO_2 has a thickness of at most 200 nm, more preferably at most 150 nm, even more preferably at most 100 nm.

[0087] In an embodiment, said at least one layer of SiO_2 has a thickness of at least 10 nm and at most 200 nm, more preferably at least 20 nm and at most 150 nm, even more preferably at least 30 nm and at most 100 nm.

Methods of measurements

[0088] It is understood that within the context of the present invention, all the atomic percentages and weight percentages above and in the claims can be determined by known techniques in the art. X-ray photoelectron spectroscopy

(XPS), and XPS depth profiling can be used in particular to determine the atomic percentages. Preferably, said article according to the present invention are profiled using a monoatomic Ar+ beam working at 2 keV and 10 μA, on a K-Alpha Thermo Scientific spectrometer (Al Kα radiation 1486.68 eV) with a spot size of 250x250 μm, and raster size of 1.25x1.25mm. To generate the profile, ten snapshot of O 1s, C 1s, Y 3d, Zr 3d and Si 2p levels have been recorded after every etch step (8 s, approximately 2 nm), at a pass energy of 150 eV. Then, the concentration of each species is derived at each step from the spectrum area of the scan, after subtraction of a Shirley background. The concentration is constant all along the depth of the coating.

[0089] It is understood that within the context of the present invention, all the thicknesses in nm can be measured by any known techniques known by the skilled in the art. Preferably, the thicknesses are measured by stylus profilometry.

Example 1

[0090] A coating was deposited on a Pt/Rh alloy substrate by means of PVD methods using 4 magnetrons. The substrate consisted of a Pt/Rh alloy having 90 at. % of Pt and 10 at. % of Rh, based on the total amounts of atoms of Pt and Rh.

[0091] The bond layer consisting of YSZ was deposited directly on the substrate by reactive sputtering of Zr and Y targets. The YSZ had a t' phase and comprised 10 at. % of yttrium, 30 at. % of zirconium, and 60 at. % of oxygen based on the total amount of atoms in said YSZ, with 5 mol.% of yttria. The Zr targets are sputtered in bipolar dual magnetron sputtering at 5A, with a ton and toff of 300 and 100 μs at 5A, with simultaneous sputtering of Y at 3.4 A, in unipolar mode, with 100μs as ton and toff, in an Ar/O_2 mixture of 90 and 60 sccm respectively, at a pressure of 10 mTorr. The bond layer had a thickness of 600 nm

[0092] The layer (L1) was deposited directly on the bond layer from a SiC/C target, using pulsed DC sputtering at 1200 W, in Ar atmosphere. The layer (L1) comprises based on the total weight of the layer (L1) at least 90 wt.% of SiC and a Si/C atomic ratio of 0.88. The obtained article thus comprised a bond layer of YSZ directly covering the substrate and a layer (L1) directly covering the bond layer. The duration of deposition for the bonding layer and layer (L1) is adapted to 3600 s and 10800 s respectively to reach 2000 nm of thickness (for the layer (L1)).

[0093] Figure 1 shows the composition of the coating, measured by XPS depth profile as explained above with the SiC on the top (0-3500s of etch time), the YSZ bond layer (3500-4500s of etch time) and the Pt/Rh substrate (4500-4800s of etch time).

[0094] The obtained coating presents an excellent thermal stability. To assess the thermal stability, the obtained article was annealed at 1100°C in ambient air during different times.

[0095] Figure 2 shows the Figure 2. XPS depth profile after annealing of 24h at 1100°C. The conditions of measurement was the same as for Figure 1.

[0096] Figure 3 shows the evolution of XRD pattern of SiC (layer (L1)) and YSZ bond layer at different annealing time at 1100°C.

[0097] Figure 4 shows the peak intensity of SiO_2 (101) and $ZrSiO_4$ (101) as a function of annealing time.

[0098] The coating, with a thickness of 2000nm, is only fully oxidized after 400h of annealing at 1100°C (YSZ was fully oxidized into $ZrSiO_4$ and the layer (L1) was fully oxidized into SiO_2). This confirms the thermal stability of the coating using XRD diffraction.

Claims

1. An article comprising:

(i) at least one substrate selected from the group consisting of Pt/Rh alloy substrate, Pt substrate, superalloys substrates, iron alloys substrates, metal carbide substrates, boron carbide substrates, boron nitride substrate, silicon nitride substrates, metal oxides substrates and combinations thereof, said substrate having at least one surface; and

(ii) one bond layer at least partially covering said surface of said substrate; said bond layer comprising yttria-stabilized zirconia, or titanium oxide, or chromium oxide; and

(iii) at least one layer (L1) at least partially covering said bonding layer; said layer (L1) comprising silicon carbide.

2. An article according to claim 1, wherein said bond layer directly covers said surface of said substrate and said layer (L1) directly covers said bond layer.

3. An article according to any of the preceding claims, wherein said titanium oxide has the formula (I):

TiO_x Formula (I)

wherein x is a rational number and is at least 1 and at most 2.

4. An article according to any of the preceding claims, wherein said yttria-stabilized zirconia has a t' phase.

5. An article according to any of the preceding claims, wherein said yttria-stabilized zirconia comprises at least 5 at. %, more preferably at least 7 at. %, even more preferably at least 8 at. % of yttrium and at most 15 at. %, more preferably at most 13 at. %, even more preferably at most 12 at. % of yttrium, based on the total amount of atoms in said yttria-stabilized zirconia.

6. An article according to any of the preceding claims, wherein said yttria-stabilized zirconia comprises at least 20 at. %, more preferably at least 25 at. % of zirconium, based on the total amount of atoms in said yttria-stabilized zirconia and at most 40 at. % of zirconium, preferably at most 35 at. % of zirconium, based on the total amount of atoms in said yttria-stabilized zirconia.

7. An article according to any of the preceding claims, wherein said yttria-stabilized zirconia comprises at least 50 at. % of oxygen, more preferably at least 55 at. % of oxygen, and at most 70 at. % of oxygen, more preferably at most 65 at. % of oxygen, based on the total amount of atoms in said yttria-stabilized zirconia.

8. An article according to any of the preceding claims, wherein said yttria-stabilized zirconia comprises at least 3 mol. % and preferably at most 6 mol. % of yttria, based on the total moles of zirconia and yttria in said yttria-stabilized zirconia.

9. An article according to any of the preceding claims, wherein said chromium oxide has the formula (II):

Cr_yO_z Formula (II)

wherein y is an integer of at least 1 and at most 8 and z is a rational number of at least 1 and at most 21.

10. An article according to any of the preceding claims, wherein said chromium oxide is selected from the group consisting of CrO, Cr_2O_5, Cr_2O_3, CrO_2, CrOs, CrOs, Cr_3O_8, Cr_BO_{21}, $Cr_2O_{2.8}$ and mixtures thereof.

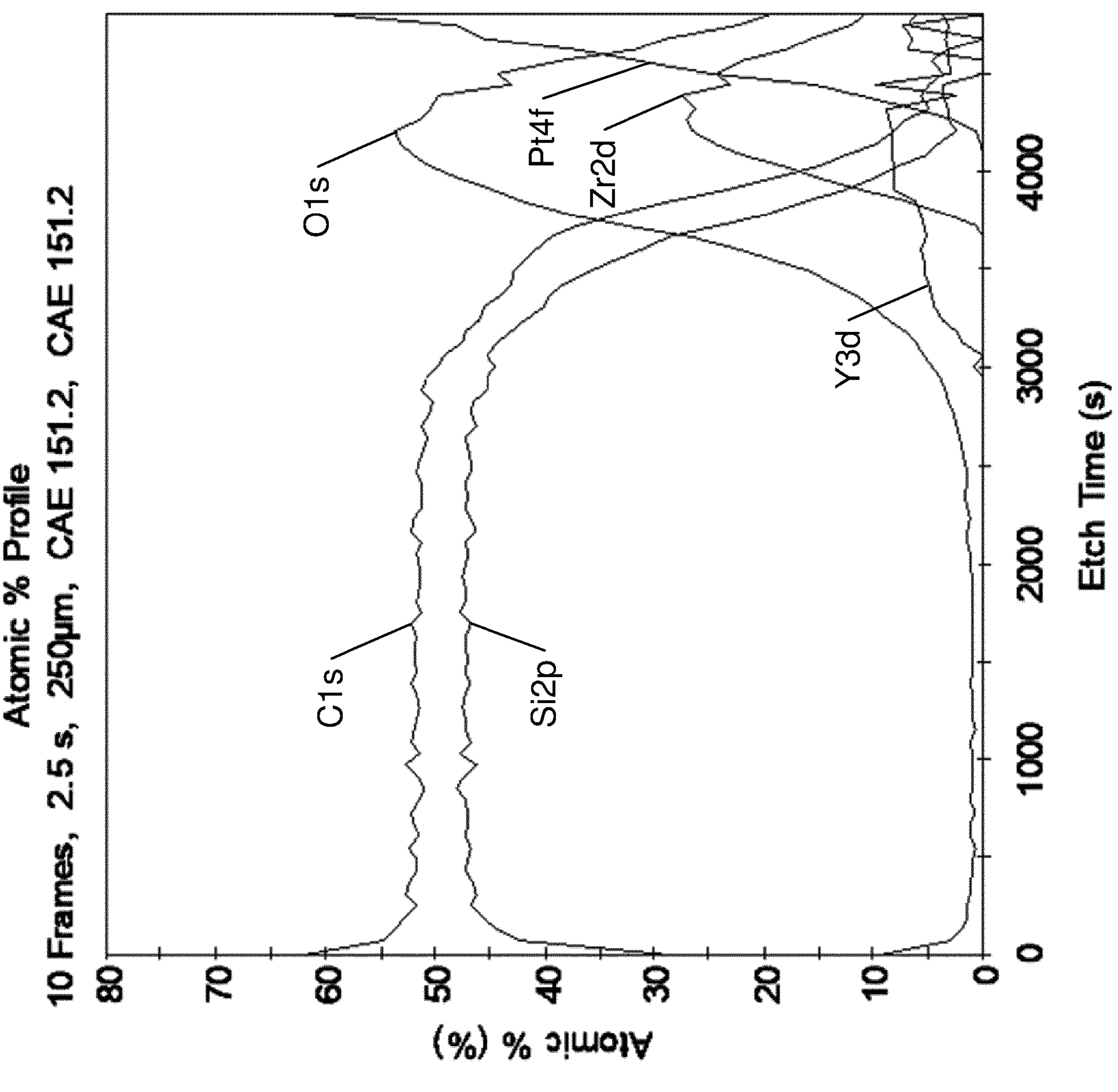
11. An article according to any of the preceding claims, wherein said bond layer comprises at least 90 wt.%, more preferably at least 95 wt.%, even more preferably at least 99 wt.%, even more preferably at least 99.9 wt.% of yttria-stabilized zirconia (YSZ), titanium oxide, or chromium oxide, based on the total weight of said bond layer.

12. An article according to any of the preceding claims, wherein said at least one layer (L1) comprises based on the total weight of said layer (L1), at least 50 wt.%, preferably at least 60 wt.%, more preferably at least 75 wt.%, even more preferably at least 80 wt.%, even more preferably at least 85 wt.%, even more preferably at least 90 wt.%, even more preferably at least 95 wt.%, even more preferably at least 99.9 wt.% of silicon carbide.

13. An article according to any of the preceding claims, wherein said at least one layer (L1) has a Si/C atomic ratio of at least 0.60, more preferably at least 0.7, even more preferably at least 0.8.

14. An article according to any of the preceding claims, wherein said at least one layer (L1) has a Si/C atomic ratio of at most 2.00, more preferably at most 1.60, even more preferably at most 1.10.

15. An article according to any of the preceding claims, wherein said at least one layer (L1) further comprises at least 1 at. %, more preferably at least 2 at. %, even more preferably at least 3 at. %, even more preferably at least 5 at. % of C and at most 15 at. %, more preferably at most 12 at. %, even more preferably at most 10 at. % of C.



Atomic % Profile
10 Frames, 2.5 s, 250µm, CAE 151.2, CAE 151.2
Atomic % (%)
Etch Time (s)
0
10
20
30
40
50
60
70
80
1000
2000
3000
4000
C1s
Si2p
O1s
Pt4f
Zr2d
Y3d

Fig. 1

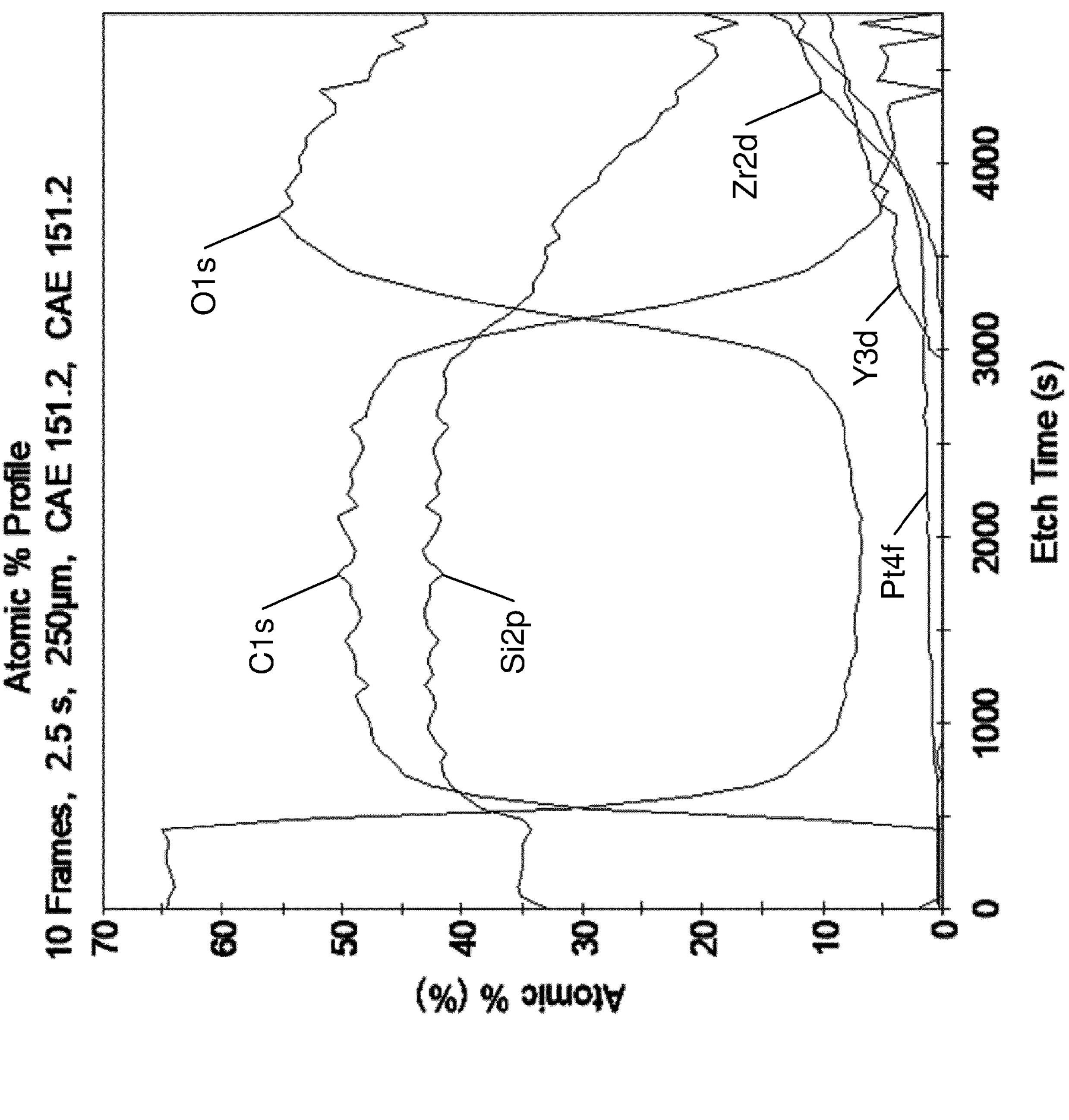

Atomic % Profile
10 Frames, 2.5 s, 250µm, CAE 151.2, CAE 151.2
Atomic % (%)
Etch Time (s)
0
10
20
30
40
50
60
70
0
1000
2000
3000
4000
O1s
C1s
Si2p
Zr2d
Y3d
Pt4f

Fig. 2

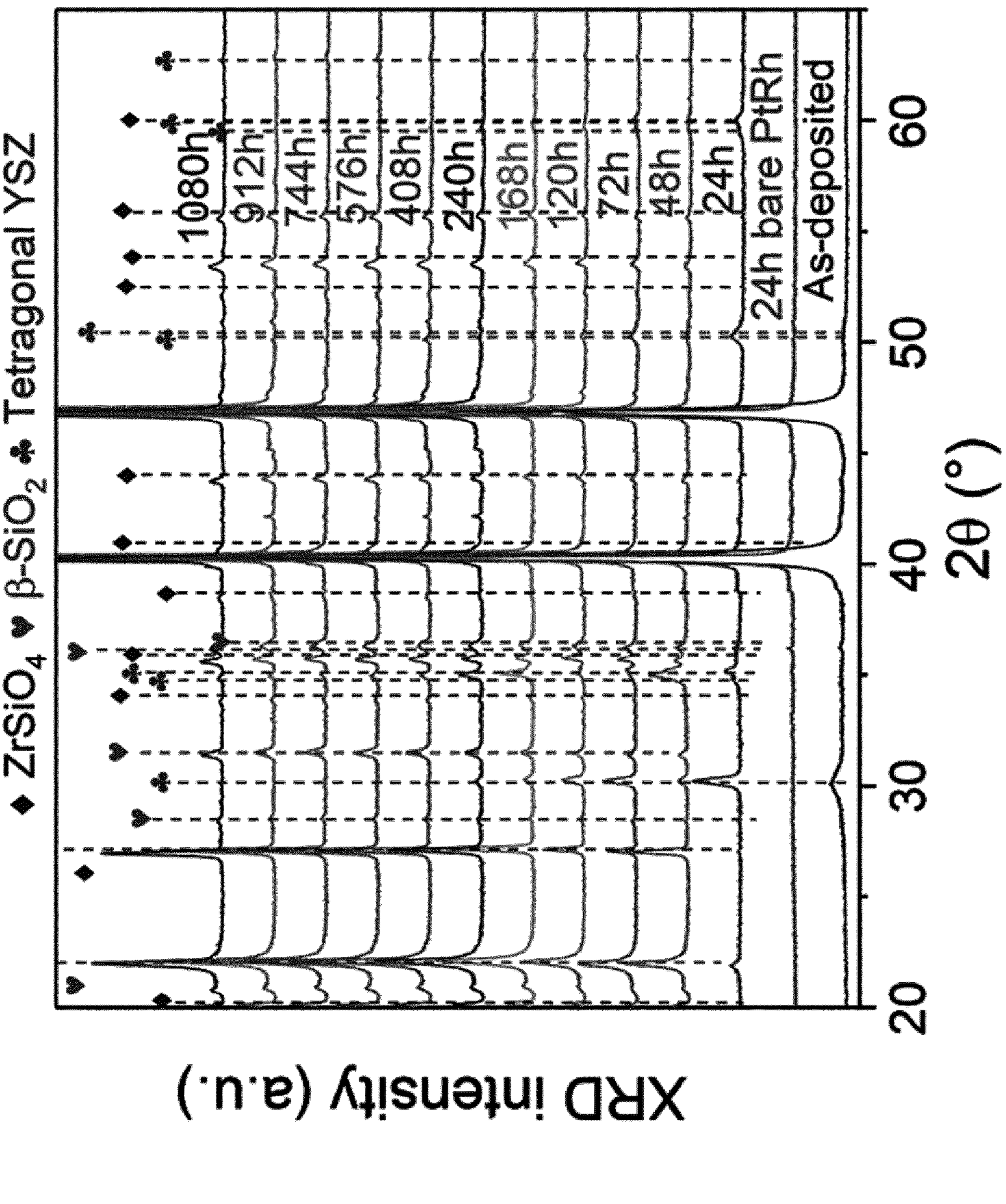

◆ ZrSiO4 ♥ β-SiO2 ♣ Tetragonal YSZ
1080h
912h
744h
576h
408h
240h
168h
120h
72h
48h
24h
24h bare PtRh
As-deposited
20
30
40
50
60
2θ (°)
XRD intensity (a.u.)

Fig. 3

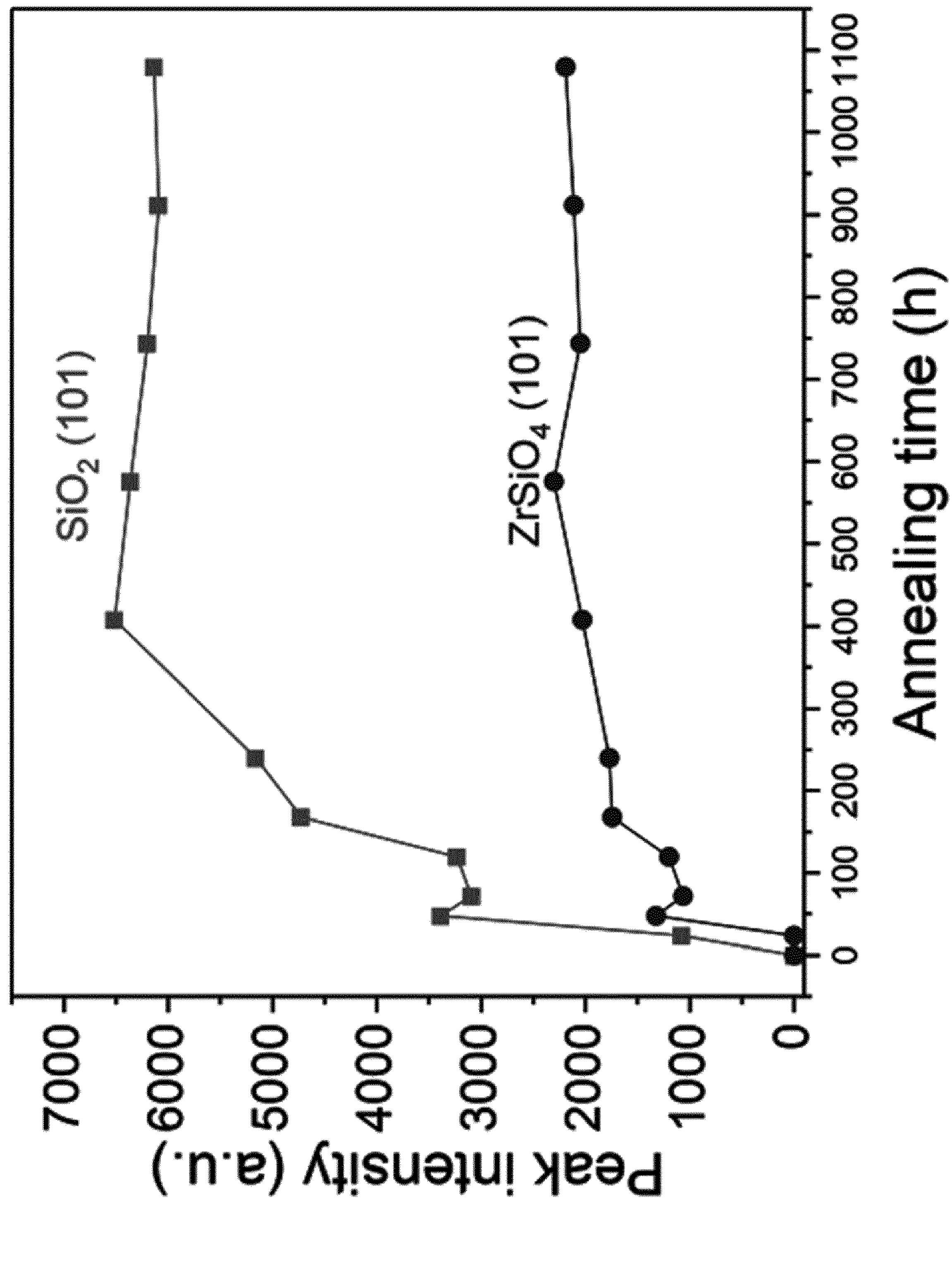

SiO2 (101)
ZrSiO4 (101)
Peak intensity (a.u.)
Annealing time (h)
0
1000
2000
3000
4000
5000
6000
7000
0
100
200
300
400
500
600
700
800
900
1000
1100

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 23 16 8761

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	US 6 299 988 B1 (WANG HONGYU [US] ET AL) 9 October 2001 (2001-10-09) * column 4, lines 17-22 * * column 5, lines 41-51 *	1-15	
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F01D
C23C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	20 September 2023	Pileri, Pierluigi

CATEGORY OF CITED DOCUMENTS

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20-09-2023

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