

Metal substrate with an oxide layer and an improved anchoring layer

In accordance with Rule 4.14 PCT, this application is a
5 Continuation-In-Part of International Application PCT/EP
96/01564, filed April 12th, 1996 and designating the USA, in
the United States of America.

The invention relates to a metal substrate with a second
10 oxide layer and an anchoring layer disposed therebetween.
More specifically, the invention relates to a superalloy
substrate with a thermal barrier layer and a layer anchoring
the thermal barrier layer onto the substrate.

15 U.S. Patent Nos. 4,055,705 to Stecura et al.; 4,321,310 to
Ulion et al.; and 4,321,311 to Strangman disclose coating
systems for gas turbine components made from nickel or
cobalt-based superalloys. A coating system described compri-
ses a thermal barrier layer made from ceramic, which in
20 particular has a columnar grained structure, placed on a
bonding layer or bond coating which in its turn is placed on
the substrate and bonds the thermal barrier layer to the
substrate. The bonding layer is made from an alloy of the
MCrAlY type, namely an alloy containing chromium, aluminum
25 and a rare earth metal such as yttrium in a base comprising
at least one of iron, cobalt and nickel. Further elements can
also be present in an MCrAlY alloy; examples are given below.
An important feature of the bonding layer is that a thin
oxide layer of alumina or a mixture of alumina and chromium
30 oxide, as dependent on particulars of the composition of the
MCrAlY alloy, inter alia, is developed on the MCrAlY alloy in
an oxidizing environment below the thermal barrier layer.

Accordingly, a bond between the thermal barrier layer and the alumina layer must be provided.

U.S. Patent No. 5,238,752 to Duderstadt et al. discloses a
5 coating system for a gas turbine component which also
incorporates a ceramic thermal barrier layer and an bonding
layer bonding the thermal barrier layer to the substrate. The
bonding layer is made from an intermetallic aluminide com-
pound, in particular a nickel aluminide or a platinum alumi-
10 nide. The bonding layer also has a thin oxide layer which
must serve to anchor the thermal barrier layer.

U.S. Patent No. 5,262,245 to Ulion et al. describes a result
of an effort to simplify coating systems incorporating ther-
15 mal barrier layers for gas turbine components by avoiding
bonding layers. To this end, a composition for a superalloy
is disclosed which may be used to form a substrate of a gas
turbine component and which develops an alumina layer on its
outer surfaces under a suitable treatment. That alumina layer
20 is used to anchor a ceramic thermal barrier layer directly on
the substrate, eliminating the need for a special bonding
layer to be placed between the substrate and the thermal bar-
rier layer.

25 U.S. Patent No. 5,087,477 to Giggins et al. shows a method
for placing a ceramic thermal barrier layer on a gas turbine
component by a physical vapor deposition process. That
process comprises establishing an atmosphere having a con-
trolled content of oxygen at the component to receive the
30 thermal barrier layer, evaporating compounds with an electron
beam and forming a gas phase, and precipitating the gas phase
on the compound to form the thermal barrier layer.

U.S. Patent Nos. 5,154,885; 5,268,238; 5,273,712; and 5,401,307 to Czech et al. disclose advanced coating systems for gas turbine components comprising protective coatings of MCrAlY alloys. The MCrAlY alloys disclosed have carefully balanced compositions to give exceptionally good resistance to corrosion and to oxidation, as well as an exceptionally good compatibility (mechanical, chemical) to the superalloys used for the substrates. The basis of the MCrAlY alloys is formed by nickel and/or cobalt. Additions of further elements, in particular silicon and rhenium, are also discussed. Rhenium in particular is shown to be a very advantageous additive. All MCrAlY alloys shown are also very suitable as bonding layers for anchoring thermal barrier layers on gas turbine components. U.S. Patent No. 5,401,307 also contains a survey over compositions of superalloys which are useful for forming gas turbine components.

A standard practice in bonding an oxide layer, in particular a thermal barrier layer, to an article of manufacture is placing an anchoring layer consisting of alumina on the article, either by placing a suitable bonding layer on the article which develops the alumina on its surface under oxidizing conditions or by selecting a material for the article which is itself capable of developing alumina on its surface. The thermal barrier layer is placed on the bonding layer and bonded to the substrate via the anchoring layer.

The thermal barrier layer itself is expediently made from an oxide ceramic, particularly stabilized or partly stabilized zirconia. "Partly Stabilized Zirconia" classifies a family of preparations containing zirconia as a principal constituent and at least one other compound which is thoroughly mixed with the zirconia and which inhibits the zirconia to change its crystalline properties under thermal cycling. Examples

for such other compounds are yttria, calcia, magnesia, ceria and lanthana; to produce the desired effect, these other compounds have to be admixed to the zirconia in amounts up to 10 percent by weight or even more. Examples are available from
5 the cited documents of the state of the art.

Particulars of the bonding of the thermal barrier layer to an anchoring layer consisting essentially of alumina have not yet attained considerable recognition or even discussion from
10 the technicians working in the field. More or less it has been taken for granted that the alumina, being a ceramic itself and being developed as a layer bonded to a suitable metal substrate, would assure bonding between the metal substrate and a thermal barrier layer placed upon the alumina
15 by its mere existence. Heretofore, only an alumina layer has been given consideration to anchor a thermal barrier layer on a superalloy substrate regardless of its declining bonding capability and increasing spalling probability as it grows during operation due to the exposure to an oxidizing environ-
20 ment. Such growth must be expected to occur at a gas turbine component under high thermal load in an oxidizing environment.

Further enquiries by the inventor have turned out that it is
25 not the mere existence of an alumina anchoring layer which bonds a thermal barrier layer placed thereon thereto, but that it is a solid state chemical reaction occurring between the alumina and the thermal barrier layer which creates a thin mixing zone between the anchoring layer and the thermal
30 barrier layer where compounds formed from both the anchoring layer and the thermal barrier layer provide for bonding.

It is accordingly an object of the invention to provide a metal substrate with an oxide layer and an improved anchoring

layer, which overcomes the above-mentioned disadvantages of the heretofore-known devices and methods of this general type and improves the bonding of the oxide layer, particularly a ceramic thermal barrier layer, to a substrate through an anchoring layer by modifying the anchoring layer in a suitable manner.

With the foregoing and other objects in view there is provided, in accordance with the invention, an article of manufacture, comprising: a metal substrate having a surface and being capable to develop a first oxide layer on the surface and tightly bonded thereto, the first oxide layer comprising a first metallic element; an anchoring layer disposed on the substrate, the anchoring layer comprising a ternary oxide formed with the first metallic element, a second metallic element and oxygen; and a second oxide layer disposed on the anchoring layer, the second oxide layer containing an oxide of the second metallic element.

With the foregoing and other objects in view there is also provided, in accordance with the invention, an article of manufacture, comprising: a substrate having a surface formed by a first oxide which comprises a first metallic element; an anchoring layer comprising a ternary oxide formed with the first metallic element, a second metallic element and oxygen; and a second oxide layer disposed on the anchoring layer and bonded to the surface by the anchoring layer, the second oxide layer containing an oxide of the second metallic element.

In accordance with an added mode of the invention, the anchoring layer comprises the ternary oxide as a principal constituent, or it consists essentially of the ternary oxide. The term "principal constituent" is understood to refer to a com-

position of matter wherein the component mentioned is present in an amount exceeding 50%, as measured in parts by weight.

In accordance with another mode of the invention, the ternary
5 oxide is selected from the group consisting of spinels, pyro-
chlores and perovskites. These three terms specify ternary
oxides by their composition as well as by their cristallogra-
phic structure. Particularly, a spinel has a chemical compo-
sition AB_2O_4 , a pyrochlore has a composition $B_2C_2O_7$ and a
10 perovskite has a composition ABO_3 . Therein, A denotes a di-
valent metal, B denotes a trivalent metal and C denotes a
tetravalent metal; O denotes oxygen. Examples of spinels and
pyrochlores are $YbAl_2O_4$, $MgAl_2O_4$, $CaAl_2O_4$; $Al_2Zr_2O_7$. All ternary
oxides mentioned explicitly or by a general formula as are
15 known as such.

In accordance with an additional mode of the invention, the
second metallic element is zirconium, and the second oxide
layer may contain zirconia as a principal constituent, and
20 particularly, the second oxide layer consists essentially of
a partly stabilized zirconia. In this context, it is particu-
larly preferred that the first metallic element is aluminum,
and that the ternary oxide is a pyrochlore formed of alumi-
num, zirconium and oxygen. A major motive for this preference
25 is the fact that the pyrochlore formed of aluminum, zirconium
and oxygen has been observed to occur at a boundary between a
layer of alumina and a layer of zirconia and indeed provides
for the bonding between these two compounds. Accordingly, the
provision of an anchoring layer formed of that pyrochlore can
30 be expected to provide good bonding properties as experienced
within the prior art which will be reliably be preserved even
if additional alumina is formed between the anchoring layer
and the substrate, as must be expected for an article which
serves as a gas turbine component under heavy load.

In accordance with a further mode of the invention, the anchoring layer is doped with nitrogen, preferably in an amount between 1 and 10 atom percent.

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In accordance with again an additional mode of the invention, the substrate is formed of a nickel or cobalt-based super-alloy.

- 10 In accordance with yet an added mode of the invention, a bonding layer is interposed between the substrate and the anchoring layer. The bonding layer is preferably formed of a material selected from the group consisting of metal aluminides and MCrAlY alloys, and it has a preferable thickness of
15 less than 25 micrometers.

- In a preferred embodiment, the substrate, the anchoring layer and the second oxide layer together form a gas turbine component. Such a component comprises in particular a mounting
20 portion for holding the component in operation and an active portion subject to a hot gas stream streaming along the component in operation, the active portion being at least partly covered by the anchoring layer and the second oxide layer. The component may in particular be formed as a blade, a vane
25 or a heat shield part.

- With the above-mentioned and other objects in view there is also provided, in accordance with the invention, a method of bonding a second oxide layer to an article of manufacture
30 formed of a metal substrate having a surface and being capable to develop a first oxide layer tightly bonded to the surface, the first oxide layer comprising a first metallic element, the method which comprises:

placing an anchoring layer on the surface, the anchoring layer comprising a ternary oxide formed with the first metallic element, the second metallic element and oxygen; placing the second oxide layer on the anchoring layer; and
5 bonding the second oxide layer to the substrate via the anchoring layer.

With the above-mentioned and other objects in view there is also provided, in accordance with the invention, a method of
10 bonding a second oxide layer comprising a second metallic element to an article of manufacture which comprises a substrate having a surface formed by a first oxide which comprises a first metallic element, the method which comprises: placing an anchoring layer on the surface, the anchoring
15 layer comprising a ternary oxide formed with the first metallic element, the second metallic element and oxygen; placing the second oxide layer on the anchoring layer; and bonding the second oxide layer to the substrate via the anchoring layer.

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In accordance with an added mode of the invention, the step of bonding the second oxide layer to the substrate is effected by subjecting the substrate with the various layers placed thereon to a suitably selected elevated temperature.
25 Thereby, solid state chemical reactions are effected at respective boundaries between a layer and the substrate or between two layers, creating the desired bonds. Eventually, that subjecting to the elevated temperature can be performed concurrently with the step of placing the second oxide layer.

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In accordance with yet an added mode of the invention, the anchoring layer is placed by: establishing an atmosphere containing oxygen around the article; evaporating a compound of the first metallic element and a compound of the second me-

tallic element into the atmosphere and forming a ternary gas phase containing the first metallic element, the second metallic element and the oxygen; and precipitating the ternary gas phase on the article.

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The compound of the first metallic element to be evaporated is preferably selected from the group consisting of the first metallic element itself and an oxide or oxides of the first metallic element. The compound of the second metallic element
10 is preferably an oxide of the second metallic element.

In accordance with again a further mode of the invention, at least one of the compound of the first metallic element and the compound of the second metallic element is evaporated by
15 irradiating at least one solid target containing the respective compound with an electron beam.

In a further development of the invention, the step of placing the anchoring layer comprises: initially establishing
20 the atmosphere containing oxygen at a given partial pressure; and evaporating the compound of the first metallic element and the compound of the second metallic element, forming the ternary gas phase and precipitating the ternary gas phase on the article while concurrently lowering the partial pressure
25 of the oxygen in the atmosphere. The second oxide layer is then placed as follows: establishing another atmosphere containing oxygen around the article; evaporating a compound with the second metallic element and forming an oxide gas phase; precipitating the oxide gas phase on the anchoring
30 layer; and reacting the anchoring layer with oxygen from the atmosphere and oxygen from the oxide gas phase precipitating on the anchoring layer.

In accordance with yet a further mode of the invention, the step of placing the second oxide layer comprises evaporating a compound with the second metallic element and forming an oxide gas phase; and precipitating the oxide gas phase on the
5 anchoring layer.

In accordance with a concomitant mode of the invention, the step of placing the anchoring layer comprises doping the anchoring layer with nitrogen. Thereby, the anchoring layer is
10 made an efficient diffusion barrier to prevent migration of diffusion active elements through the anchoring layer into the second oxide layer. The doping can in particular be performed by placing the anchoring layer by PVD or a similar process in an atmosphere containing an amount of nitrogen or
15 by heat treating the anchoring layer after its placing in an atmosphere containing nitrogen to diffuse nitrogen into the anchoring layer.

Other features which are considered as characteristic for the
20 invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in a metal substrate with an oxide coating and an improved anchoring layer, it is nevertheless not intended to
25 be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

30 The construction of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of the specific embodiment when read in connection with the accompanying drawings. In the drawings:

Fig. 1 is a fragmentary cross-sectional view of a substrate with a protective coating system incorporating a second oxide layer and an anchoring layer; and

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Fig. 2 is a perspective view of a gas turbine airfoil component comprising the substrate and the protective coating system shown in Fig. 1.

10 Referring now to the figures of the drawing in detail and first, particularly, to Fig. 1 thereof, there is seen a substrate 1 of an article of manufacture, in particular a gas turbine component, which in operation is subject to a heavy thermal load and concurrently to corrosive and erosive at-
15 tack, including an attack by oxidation. The substrate 1 is formed of a material which is suitable to provide strength and structural stability when subjected to a heavy thermal load and eventually an additional mechanical load by severe forces like centrifugal forces. A material which is widely
20 recognized and employed for such a purpose in a gas turbine engine is a nickel or cobalt-based superalloy. Preferred examples of such superalloys are nickel-based superalloy IN738LC and cobalt-based superalloy MAR-M 509, as specified according to common practice.

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In order to limit the thermal load imposed on the substrate 1, it has a thermal barrier layer in the form of a second oxide layer 2 placed thereon. This second oxide layer 2 is made from a columnar grained oxide ceramic, in particular
30 consisting essentially of a stabilized or partly stabilized zirconia as explained above. The second oxide layer 2 is anchored to the substrate 1 by means of an anchoring layer 3. This anchoring layer 3 is developed on a bonding layer 4 which has to be placed on the substrate 1 priorly. The bon-

ding layer 4 consists of an MCrAlY alloy and preferably of an MCrAlY alloy as patented in one of the US Patents 5,154,885, 5,268,238, 5,273,712 and 5,401,307. The drawing is not intended to show the thicknesses of the layers 3 and 4 to scale; the thickness of the anchoring layer 3 might in reality be very much less than the thickness of the bonding layer 4 and amount only to a few layers of atoms, as specified hereinabove.

- 10 The anchoring layer 3 consists essentially of a pyrochlore formed with a first metallic element, namely aluminum, and a second metallic element whose oxide constitutes at least partly the second oxide layer 2, namely zirconium. That pyrochlore is chemically and crystallographically affine to the material forming the second oxide layer 2 as well as to the material forming the portion of the article located immediately below the anchoring layer 3, namely the bonding layer 4 which in its turn is affine to alumina due to its capability to develop an alumina layer tightly bonded to it, or an alumina layer tightly bonded to the bonding layer 4 and developed thereon under exposure to an oxidizing environment. Thus, the anchoring layer 3 forms a preferred interface between the oxide layer 2 and the part of the article located below the anchoring layer 3, in the embodiment shown the bonding layer 4 resp. an alumina layer emerging from the bonding layer 4 under oxidizing conditions.

- The anchoring layer 3 can in particular be placed by a physical vapor deposition (PVD) process, preferably by electron beam PVD and in an oxygen-containing atmosphere. Such a process is in particular carried out while holding the substrate 1 at a temperature of about 700°C. Furthermore, it may be advantageous to place the anchoring layer 3 with an oxygen deficiency and react that anchoring layer 3 with addi-

tional oxygen during placing of the second oxide layer 2, which is then to be done in another atmosphere containing oxygen.

- 5 Most preferred is a mode of placing the anchoring layer 3 by precipitating a few layers of atoms with an almost stoichiometric composition and placing the rest of the anchoring layer 3 with an oxygen deficiency. This is expediently done by initially providing an atmosphere which is relatively rich
10 in oxygen, preferably complying with the specification given above. The presence of oxygen in a relatively high amount gives rise to chemical reactions with the constituents of the material located immediately below the anchoring layer 3, thus providing a tight bonding of the anchoring layer 3. Sub-
15 sequently, the oxygen content of the atmosphere is lowered, particularly by reducing the total pressure of the atmosphere. The oxygen deficiency in the anchoring layer 3 thus occurring is relieved afterwards by a chemical reaction with the constituents of the second oxide layer 2 and with oxygen
20 provided as the second oxide layer 2 is placed. This gives a tight bond to the second oxide layer 2 as well. The thickness of the anchoring layer 3 is preferably kept below 25 micrometers (μm).
- 25 The second oxide layer 2 may be placed on the anchoring layer 3 immediately after placing the anchoring layer 3, and in particular by making use of previously used apparatus to the largest possible extent. This may apply in particular if the second oxide layer 2 is also placed by PVD.
- 30 The placing of the second oxide layer 2 by means other than PVD is of course also possible. In particular, it is possible to place the second oxide layer 2 by atmospheric plasma spraying.

As a further improvement, it is also contemplated to dope the anchoring layer 3 with nitrogen, thereby providing a nitrogen content between 1 and 10 atom percent, particularly between 2 and 5 atom percent. The nitrogen provides certain slight charge imbalances and spatial distortions in the ternary oxide's crystal lattice and thereby renders it opaque or impenetrable for other elements. Thereby, transmission of diffusion active elements like hafnium, titanium, tungsten and silicon from the substrate 1 or the bonding layer 4 into the second oxide layer 2 can be prevented. That measure is particularly suitable if the second oxide layer 2 is a zirconia compound, since almost every zirconia compound must have an admixture of a further compound to stabilize its pertinent properties. Further elements penetrating into the zirconia compound might well impart the stabilization and thus question its long term efficiency, particular when used as a thermal barrier layer. The nitrogen doping of the anchoring layer 3 is well suited to ensure a long term efficiency of the second oxide layer 2. The nitrogen doping of the anchoring layer 3 can be provided concurrently with its placing, particularly by PVD in an atmosphere which contains an efficient amount of nitrogen. In this context, all PVD processes just described are applicable, by using atmospheres containing nitrogen besides oxygen. It is also possible to dope the anchoring layer 3 after its placing, particularly by a heat treatment in an atmosphere containing an efficient amount of nitrogen and diffusing the nitrogen into the anchoring layer 3.

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Fig. 2 shows the whole gas turbine component, namely a gas turbine airfoil component 5, in particular a turbine blade. The component 5 has an airfoil portion 6, which in operation forms an "active part" of the gas turbine engine, a mounting

portion 7, at which the component 5 is fixedly held in its place, and a sealing portion 8, which forms a seal together with adjacent sealing portions of neighboring components to prevent an escape of a gas stream 9 flowing along the airfoil portion 6 during operation.

The location of the arrangement shown in Fig. 1 is indicated by the section line I-I.

10 Referring again to Fig. 1, particular advantages of the novel combination of the anchoring layer 3 and the second oxide layer 2 can be summarized as follows: The anchoring layer 3 has a composition which has similarities to the second oxide layer 2 as well as to the bonding layer 4 and is tightly bonded to both layers by solid-state chemical reactions. It provides for a smooth and graded transition between the material of the second oxide layer 2 and an alumina layer developing between the anchoring layer 3 and the substrate 1 or the bonding layer 4 and yet retains the tight bonds provided by the solid-state reactions. The anchoring layer 3 can be deposited independently from the second oxide layer 2. Oxidizing the substrate 1 or the bonding layer 4 eventually deposited thereon prior to putting the component to operation can be avoided, thereby lengthening the available lifetime of the component considerably. The combination of the anchoring layer 3 and the second oxide layer 2 thus made has all advantages of such combinations known from the prior art and additionally has a substantially prolonged lifetime.



Claims

1. An article of manufacture, comprising:
a metal substrate having a surface and being capable to
5 develop a first oxide layer on said surface and tightly
bonded thereto, said first oxide layer comprising a first
metallic element;
an anchoring layer disposed on said surface, said anchoring
layer comprising a ternary oxide formed with said first
10 metallic element, a second metallic element and oxygen; and
a second oxide layer disposed on said anchoring layer, said
second oxide layer containing an oxide of said second
metallic element.
- 15 2. An article of manufacture, comprising:
a substrate having a surface formed by a first oxide which
comprises a first metallic element;
an anchoring layer disposed on said surface, said anchoring
layer comprising a ternary oxide formed with said first
20 metallic element, a second metallic element and oxygen; and
a second oxide layer disposed on said anchoring layer and
bonded to said surface by said anchoring layer, said second
oxide layer containing an oxide of said second metallic
element.
- 25 3. The article according to claim 1 or claim 2, wherein said
anchoring layer comprises said ternary oxide as a principal
constituent.
- 30 4. The article according to claim 1 or claim 2, wherein said
anchoring layer consists essentially of said ternary oxide.
5. The article according to one of the preceding claims,
wherein said ternary oxide is selected from the group
35 consisting of spinels, pyrochlores and perovskites.



6. The article according to one of the preceding claims, wherein said first metallic element is aluminum.

5 7. The article according to one of the preceding claims, wherein said second metallic element is zirconium.

8. The article according to claim 7, wherein said second oxide layer contains zirconia as a principal constituent.

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9. The article according to claim 7, wherein said second oxide layer consists essentially of a partly stabilized zirconia.

15 10. The article according to one of claims 7 to 9, wherein said first metallic element is aluminum, and wherein said ternary oxide is a pyrochlore formed of aluminum, zirconium and oxygen.

20 11. The article according to one of the preceding claims, wherein said anchoring layer is doped with nitrogen.

12. The article according to claim 11, wherein said nitrogen is present in said anchoring layer in an amount between 1 and
25 10 atom percent.

13. The article according to one of the preceding claims, wherein said substrate is formed of a nickel or cobalt-based superalloy.

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14. The article according to one of the preceding claims, comprising a metallic bonding layer interposed between said substrate and said anchoring layer and having said surface defined on said bonding layer.



15. The article according to claim 14, wherein said bonding layer is formed of a material selected from the group consisting of metal aluminides and MCrAlY alloys.

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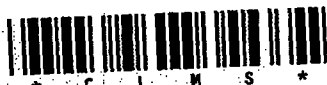
16. The article according to one of the preceding claims, wherein said anchoring layer has a thickness of less than 25 micrometers.

10 17. The article according to one of the preceding claims, wherein said substrate, said anchoring layer and said second oxide layer form a gas turbine component.

15 18. The article according to claim 17, wherein said gas turbine component comprises a mounting portion for holding the component in operation and an active portion subject to a hot gas stream streaming along the component in operation, said active portion being at least partly covered by said anchoring layer and said second oxide layer.

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19. A method of bonding a second oxide layer comprising a second metallic element to an article of manufacture formed of a metal substrate having a surface and being capable to develop a first oxide layer tightly bonded to the surface,
25 the first oxide layer comprising a first metallic element, the method which comprises:
placing an anchoring layer on the surface, the anchoring layer comprising a ternary oxide formed with the first metallic element, the second metallic element and oxygen;
30 placing the second oxide layer on the anchoring layer; and bonding the second oxide layer to the substrate via the anchoring layer.



20. A method of bonding a second oxide layer comprising a second metallic element to an article of manufacture formed of a substrate having a surface formed by a first oxide layer which comprises a first metallic element, the method which

5 comprises:

placing an anchoring layer on said surface, the anchoring layer comprising a ternary oxide formed with the first metallic element, the second metallic element and oxygen; placing the second oxide layer on the anchoring layer; and

10 bonding the second oxide layer to the substrate via the anchoring layer.

21. The method according to claim 19 or claim 20, wherein the step of bonding the second oxide layer to the substrate

15 comprises subjecting the substrate with the layers placed thereon to an elevated temperature.

22. The method according to one of claims 19 to 21, wherein the step of placing the anchoring layer comprises:

20 establishing an atmosphere containing oxygen around the article;

evaporating a compound of the first metallic element and a compound of the second metallic element into the atmosphere and forming a ternary gas phase containing the first metallic

25 element, the second metallic element and the oxygen; and precipitating the ternary gas phase on the article.

23. The method according to claim 22, which comprises evaporating the compound of the first metallic element as

30 selected from the group consisting of the first metallic element and an oxide of the first metallic element.

24. The method according to claim 22 or claim 23, which comprises evaporating the compound of the second metallic



element as selected to be an oxide of the second metallic element.

25. The method according to one of claims 22 to 24, which
5 comprises evaporating at least one of the compound of the first metallic element and the compound of the second metallic element by irradiating at least one solid target containing the respective compound with an electron beam.
- 10 26. The method according to one of claims 22 to 25, wherein the step of placing the anchoring layer comprises:
initially establishing the atmosphere containing oxygen at a given partial pressure; and
evaporating the compound of the first metallic element and
15 the compound of the second metallic element, forming the ternary gas phase and precipitating the ternary gas phase on the article while concurrently lowering the partial pressure of the oxygen in the atmosphere;
and wherein the step of placing the second oxide layer
20 comprises:
establishing another atmosphere containing oxygen around the article;
evaporating a compound with the second metallic element and forming an oxide gas phase;
25 precipitating the oxide gas phase on the anchoring layer; and reacting the anchoring layer with oxygen from the atmosphere and oxygen from the oxide gas phase precipitating on the anchoring layer.
- 30 27. The method according to one of claims 19 to 26, wherein the step of placing the second oxide layer comprises evaporating a compound with the second metallic element and forming an oxide gas phase, and precipitating the oxide gas phase on the anchoring layer.



28. The method according to one of claims 19 to 26, wherein the step of placing the anchoring layer comprises doping the anchoring layer with nitrogen.