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(54) Title: THERMAL BARRIER SYSTEMS WITH IMPROVED ADHESION

Abstract: The present invention provides strategies for making thermal barrier coating systems that protect metallic substrates in high temperature environments. The coatings show excellent adhesion to substrates as well as among layers of the coatings. The coatings generally include a first coating comprising an aluminide that is formed on the substrate. An oxide layer is formed on this first coating. A second coating comprising a ceramic is then formed on the oxide. An aspect of the present invention is that the oxide is at least partially and more preferably substantially fully formed before the ceramic topcoat is provided.
THERMAL BARRIER SYSTEMS WITH IMPROVED ADHESION

Cross-Reference to Related Application

This application claims the benefit of priority to U.S. Provisional application no. 61/868,877 filed August 22, 2013 entitled "THERMAL BARRIER SYSTEMS WITH IMPROVED ADHESION" the entire disclosure of which is incorporated herein by reference for all purposes.

Field of the Invention

The present invention relates to thermal barrier systems that help to protect metal-containing substrates in high temperature environments. More specifically, the present invention relates to thermal barrier coatings comprising an aluminum-containing base coat, an intermediate thermally grown oxide layer formed on the base coat, and a ceramic topcoat formed on the thermally grown oxide, wherein the thermal barrier system has improved durability and improved resistance to thermal degradation.

Background of the Invention

The function of a gas turbine engine is to convert the energy in hydrocarbon fuel into useful work. The gas turbine accomplishes this by compression of ambient air, addition of fuel to the compressed air, and combustion of the fuel/air mixture to drive a turbine. Good design of the engine components promotes efficient conversion of the energy into useful work. Although component design influences efficiency and power output to some degree, another primary factor affecting engine efficiency and power output is the difference between the ambient temperature of the incoming air and the combustion temperature. The correlation of efficiency and power output to this temperature difference is a principle of basic thermodynamics. This means that greater efficiency and more power generally result with increasing operating temperature of the gas directed to the turbine. In practical terms, this means that the high temperature performance of the turbine components (combustors, blades and vane segments, for example) is a major factor in increasing engine efficiency and power output of the engine.

The drive to improve engine combustion efficiency and reducing emissions has resulted in a significant increase of the Turbine Inlet Temperatures within gas-
turbine engines since the 1940s. Presently, the high-pressure turbine blades and
vanes exposed to hot gases in commercial aeronautical engines typically experience
metal surface temperatures of about 1000°C, with short-term peaks as high as
1100°C. In this service environment, significant advances in high temperature
capabilities have been achieved through the development of iron, nickel and cobalt-
based superalloys and the use of oxidation-resistant environmental coatings capable
of protecting the superalloys from oxidation, hot corrosion, etc. The superalloy
substrate often provides the basic strength of the component and carries the loads.
Further improvements in operating temperature have been achieved through
enhancements in cooling schemes such as internal cooling, film cooling, and even
transpiration cooling. Grain boundaries are a strengthening mechanism at room
temperature but can be a source of failure at elevated temperatures in some current
generation engines. Development of specialized casting techniques to control and/or
reduce grain boundaries in turbine airfoils has lead to columnar grained and single
crystal airfoils.

With the improved cooling, improved crystal structure, and improved alloy
chemistry, a limiting factor in turbine performance shifted from the material strength
to oxidation life of the components. For instance, the surfaces of the articles to be
protected can be protected with an aluminum-containing protective coating whose
surface oxidizes to form an aluminum oxide scale that inhibits further oxidation.
The protective coating therefore is sufficiently rich in Al to promote thermal growth
of this oxide scale. The scale is also referred to as a thermally grown oxide (TGO).

A conventional bond coat is typically either an MCrAlY overlay (where M is Ni, Co, Fe, or combination of them) or a diffusion aluminate coating. An MCrAlY
overlay is generally applied by Electron Beam Physical Vapor Deposition (EB-
PVD), High Velocity Oxy-Fuel (HVOF), Low Pressure Plasma Spray (LPPS) or
Vacuum Plasma Spray (VPS). Diffusion aluminate coatings are generally formed
by chemical vapor deposition (CVD), slurry coating, or by a diffusion process such
as pack cementation, above-pack, or vapor (gas) phase deposition. Diffusion
aluminide coatings have particularly found widespread use as protective coatings for
superalloy components of gas turbine engines due to: (1) the diffusion process is not
a line-of-sight process allowing components with complex geometry or with internal
surfaces to be coated; and (2) the diffusion process is generally cost-effective as compared with overlay process.

Refractory elements have been incorporated into aluminide coatings to improve the oxidation protection and adhesion properties provided by these coatings. Examples of refractory elements that have been proposed for aluminide compositions include Hf, Zr, Y, La and/or Ce. With small additions of refractory elements to aluminide coatings, the adherence of the protective oxide scale to the coatings/alloys and the oxidation resistance of the coatings/alloys at high temperature under aggressive atmospheres can be improved.

The significant improvement of oxidation resistance due to Hf addition has been indicated in many cases, such as Hf addition to β-NiAl cast alloys (Pint et al., "Effect of quaternary additions on the oxidation behavior of Hf-doped NiAl," *Oxidation of Metals*, Vol.59, Pages 257-283, 2003), and Hf addition to MCrAlY coatings materials (Giggins Jr., et al., U.S. Patent 3,993,454, and Gupta et al., U.S. Patent 4,585,481). In addition, Hf addition has also been proved that hafnium decreases the propensity for rumpling when it diffuses into the coating and to the growing aluminum oxide increasing their creep resistance (Tolpygo et al, "Effect of Hf, Y and C in the underlying superalloy on the rumpling of diffusion aluminide coatings," *Acta Materialia* 56, Pages 489^499, 2008) as well as decreases the voids formed in the coating alloy at the metal-oxide interface during oxidation (Provenzano et al., "Void formation and suppression during high temperature oxidation of MCrAlY-type coatings," Surface and Coatings Technology, 36, Pages 61-74, 1988).

Recently, U.S. Patent No. 7,273,662 to Gleeson et al. taught two-phase γ-Ni + γ’ Ni₃Al alloy compositions with a purpose of reducing the progressive roughening or "rumpling" of the bond coat surface during thermal exposure.

Due to the significant beneficial effect of Hf addition, diffusion coating processes to incorporate Hf into diffusion aluminide coatings have been studied for several decades. As early as the 1970s, U.S. Pat. No. 3,951,642 and U.S. Pat. No. 3,996,021 to Chang et al. disclosed a pack cementation process to produce Hf modified aluminide coatings. Later, U.S. Pat. No. 5,989,733, U.S. Pat. No. 6,136,451, U.S. Pat. No. 6,689,422 to Warnes et al. and U.S. Pat. No. 6,602,356 to
Nagaraj et al. disclosed a CVD process to produce Platinum (Pt)-aluminide coatings with or without Hf addition. U.S. Pat. No. 6,514,629 and U.S. Pat. No. 6,582,772 to Rigney et al. taught Hf-Si-modified Pt-aluminide coatings formed by the steps of providing a substrate, depositing layers containing the platinum, aluminum, hafnium, and silicon, and heating the layers so that the aluminum, hafnium, and silicon diffuse into the layer of platinum to form a protective layer.

Pack cementation, CVD and vapor phase process are three potential industrial diffusion coating processes for forming Hf-modified aluminide diffusion coatings. Among them, the vapor phase process has the potential to offer many advantages. The others have drawbacks. Though used with some successes, pack cementation processes for both hafnium-modified aluminide and simple aluminide coatings share the same disadvantages, such as the need for an inert filler, the obstruction of cooling holes, and the embedded particles on the formed coating surface. While avoiding these shortcomings, a significant disadvantage of using a CVD process to form a hafnium-modified aluminide coating is the considerable equipment cost. In view of these disadvantages of pack and CVD processes, alternative deposition methods, such as vapor phase process, have been sought.

U.S. Pat. No. 6,332,931 to Das et al. disclosed a vapor phase coating process to produce aluminide-hafnide coatings by using Hf metal or Hf-containing metallic alloys as Hf donor materials; as a result, the synthesized coatings contain about 0.5 to about 60 weight percent hafnium and about 12 to about 38 weight percent aluminum. However, too high Hf content in aluminide coatings can lead to the formation of Hf-rich precipitated phases in the coating or on the coating surface, such as HfC, HfO2, and Ni2AlHf etc., and furthermore, deteriorate the mechanical properties and the oxidation resistance of the aluminide coatings. Therefore, there is a need to develop low Hf content aluminide coatings whose application on turbine engine components, as either environmental coatings or the bond coat in a thermal barrier coating system, can significantly improve the gas-turbine performance. Due to the difficulty on the control over Hf and Al codeposition and the complex process parameters of the diffusion coating process, even though Hf modified aluminide coatings have been investigated for several decades, very limited information of Hf-modified aluminide diffusion coatings for industrial applications has been reported.
A significant obstacle to the use of vapor phase processes has been the inability to adequately and efficiently control the co-deposition of aluminum and refractory elements, such as Hf, from suitable sources to the article to be coated. Unfortunately, many known vapor phase processes inefficiently and inconsistently use refractory elements. This is a significant drawback not only for performance of the resultant coated articles, but also due to the relative high expense of the refractory elements. Therefore, there is a strong desire and need in the industry to be able to use vapor phase coating techniques in a way that offers improved control over the co-transfer of aluminum and refractory element(s) such as Hf.

The concept of increasing the operating temperature by changing the heat transfer characteristics of engine components also has been investigated. One strategy involves coating an additional layer onto the surface of a substrate, such as an air-cooled superalloy component, wherein the coating includes a material with a thermal conductivity less than that of the superalloy. Ceramic materials are examples of high temperature coating materials that have been used to modify heat transfer characteristics. A ceramic topcoat may be further applied over the aluminum-containing protective layer to help provide a thermal barrier that extends service life. Ceramic materials by nature have a lower thermal conductivity than metals. Surface metal temperature reductions of 250°F to 300°F are theoretically possible with a .005” to .010” thick ceramic layer and use of internal cooling. In actual practice, temperature reductions of about 100°F to 180°F are more likely to be achieved. The protective coating (also referred to as a bond coat), the TGO layer, and the optional ceramic topcoat provide a thermal barrier coating system (TBC) to protect the coated article.

Several challenges exist in applying a ceramic material to a metallic substrate. One challenge is the significant difference in coefficient of thermal expansion (CTE) between the two classes of materials. The difference in CTE characteristics undermines the adhesion between a ceramic coating and a metal substrate. The difference in CTE between the metal and the ceramic will result in very high stresses along the bond interface as the temperature increases. Cooling also causes stresses at the interface, as the metal contracts faster than the ceramic. The stresses tend to cause the ceramic coating to spall, crack, delaminate, chip, or
otherwise degrade. In addition to imparting oxidation resistance, the TGO helps bond the ceramic topcoat to the protective coating.

The spallation and cracking of the thickening TGO scale layer is another failure mechanism of conventional thermal barrier systems. Thus, improving the adhesion and integrity of the interfacial TGO scale is critical to the development of more reliable thermal barrier systems. Ideally, when exposed to high temperatures, the aluminum-containing protective coating should oxidize to form a slow-growing, non- or less "rumpling," nonporous TGO layer that adhere well to the protective coating and the ceramic topcoat.

**Summary of the Invention**

The present invention provides strategies for making aluminide coatings and corresponding thermal barrier coating systems that protect metallic substrates in high temperature environments.

The coatings show excellent adhesion to substrates as well as among layers of the coatings. The coatings generally include a first coating comprising an aluminide that is formed on the substrate. An oxide layer is formed on this first coating. A third coating comprising a ceramic is then formed on the oxide. An aspect of the present invention is that the oxide is at least partially and more preferably substantially fully formed before the ceramic topcoat is provided.

Otherwise, the oxide will form in situ between the already existing first and third coatings and then act like a wedge to break the interface between the first and third coatings.

The improvement in adhesion is dramatic. When practicing principles of the present invention, a coating can be severely stressed by sectioning with a diamond saw. Even though sectioning like this causes cut edges to be under compression or tensile stresses, very little if any chipping can be visually observed on the sectioned edges in preferred embodiments. In contrast, without practicing the principles of the present invention, sectioning causes significant chipping, cracking, and delamination in coatings in which the oxide is allowed to form later.

In some preferred embodiments, vapor phase coating techniques optionally are used in manner that efficiently and consistently incorporate refractory element content into the aluminide coatings. The coatings show excellent adhesion to
substrates as well as among layers of the coatings. The coatings generally include a first coating comprising an aluminide that is formed on the substrate. In some embodiments, an oxide layer optionally is formed on this first coating. In some embodiments, a third coating comprising a ceramic optionally is then formed on the oxide.

In this preferred aspect of the present invention, the aluminide coating deposition desirably incorporates two heating stages. A first heating stage occurs in the presence of a reducing gas under conditions that significantly increase or otherwise favor the formation of refractory element-containing species in the vapor phase. The result is that surprisingly high levels of refractory element content can be incorporated into the resultant coatings in the second stage even when the donor materials contain relatively little refractory element content. For example, refractory element donor materials are used so efficiently that donor materials that include under 1 weight percent of refractory element donor compounds based on the total weight of aluminum sources can provide coatings with over 5 weight percent of the refractory element. The process provides uniform coatings and is consistent from run to run.

The present invention may be used to apply coatings that protect any articles from a hostile operating environment. In preferred modes of practice, the coatings protect against oxidation, hot corrosion, or other degradation in high temperature and/or chemically hostile environments. A wide range of articles can be protected by these coatings, including turbine engine hot zone components, blades, vanes, combustors transition pieces, and the like.

In one aspect, the present invention relates to a method of forming a thermal barrier coating comprising:

(a) providing a substrate comprising at least one metallic surface;
(b) roughening at least a portion of the metallic surface
(c) forming a coating on at least a portion of the roughened surface of the substrate, wherein the coating comprises at least one aluminide; and
(d) treating the aluminide coating under conditions effective to form an oxide coating on the aluminide coating:
(e) after forming the oxide coating, forming a third coating on the oxide coating, said third coating comprising at least one ceramic material.

In another aspect, the present invention relates to a method of refurbishing a coated article comprising:

(a) providing an article having a metallic surface and a coating on at least a portion of the metallic surface;
(b) treating the article under conditions effective to remove at least a portion of the coating from the metallic surface, wherein said treatment roughens at least a portion of the metallic surface from which the coating is removed;
(c) forming a coating on at least a portion of the roughened surface, said coating comprising at least one aluminide;
(d) treating the aluminide coating under conditions effective to form an oxide coating on the aluminide coating;
(e) after forming the oxide coating, forming a third coating on the oxide coating, said third coating comprising at least one ceramic material.

**Brief Description of the Drawings**

The above mentioned and other advantages of the present invention, and the manner of attaining them, will become more apparent and the invention itself will be better understood by reference to the following description of the embodiments of the invention taken in conjunction with the accompanying drawings, wherein:

**FIG. 1** is a cross-sectional diagram of a metallic article with a thermal barrier coating of the present invention.

**Detailed Description of the Presently Preferred Embodiments**

The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather the embodiments are chosen and described so that others skilled in the art may appreciate and understand the principles and practices of the present invention.

**FIG. 1** schematically shows a cross-section of a portion of a coated article manufactured in accordance with principles of the present invention. In representative embodiments, article 10 is a constituent of a rocket, missile, aircraft,
marine vessel, industrial facility, power utility, electric motor, chemical manufacturing facility, heat exchanger, and/or the like. The principles of the present invention are desirably practiced in such applications where protection against oxidation in a high temperature environment, e.g., above about 450°C, preferably above about 650°C, more preferably above about 850°C, is desired. In preferred embodiments, article 10 is a constituent of a gas turbine engine such as being all or a portion of a high pressure turbine nozzle, low pressure turbine nozzle, turbine shroud, turbine blade, turbine vanes, and/or the like. Article 10 can be a new part, a replacement part, or a repaired or refurbished part. The article 10 can be casted, molded, machined, directionally solidified (DS), fabricated from a single crystal (SX), and/or fabricated in any other desired method.

The article 10 includes a body 11 that serves as a substrate for thermal barrier structure 12. Body 11 includes a metallic composition that may be a pure metal, an intermetallic composition, an alloy, combinations of these and the like. The body may contain a single phase or may contain multiple phases, e.g., an alloy matrix with intermetallic precipitates. Body 11 may be amorphous, crystalline, and/or the like. In addition to metal and/or intermetallic constituents, body 11 may also contain other constituents. For instance, body 11 may be a composite that includes a metallic matrix and fibers (not shown) or the like.

In preferred embodiments, body 11 includes nickel (Ni)-base, cobalt (Co)-base, titanium (Ti)-base, or iron (Fe)-base alloys. The term "Ni-base alloy" means that Ni is the dominant element in the alloy. That is, more Ni is present than any other individual metal element in the alloy. Similarly, Co, Ti, and Fe are the dominant element in Co-base, Ti-base, and Fe-base alloys, respectively. The alloy may include one or more other alloying elements such as chromium, aluminum, titanium, molybdenum, iron, manganese, tungsten, boron, niobium, tantalum, cobalt, silicon, rhenium, platinum, hafnium, zirconium, yttrium, combinations of these and the like. In some embodiments, alloys of nickel, cobalt, and/or nickel-iron (with or without other alloying elements) are known as superalloys due to excellent mechanical strength, creep resistance and good surface stability at high temperatures. Examples of superalloys are available under trade designations including HASTELLOY X, INCONEL 738, INCONEL 100, INCONEL 713,
INCONEL 792, INCONEL 792-DS, INCONEL 792-SX, INCONEL 939, WASPALOY™, RENE™ (e.g. RENE 41, RENE 80, RENE 95, and RENE 141), HAYNES-188, HAYNES-L605, INCOLOY™, MP98T, TMS, X40, MAR-M-247, CMSX-4, and CMSX-6.

Optionally, body 11 may include one or more layers. For instance, in some instances, a layer of platinum (not shown) may be deposited to form a surface layer on at least a portion of body 11. At high temperatures, the platinum can diffuse and incorporate into the protective coating 13 so that such separate layer of platinum may have dissipated at least into coating 13 after some period of use. In many embodiments, platinum can help to enhance the oxidation protection of body 11. The incorporation of platinum also can enhance the mechanical properties of the aluminide coatings. Optionally, all or selected portion(s) of body 11 can be coated with a layer comprising Pt and heat treated. The platinum can be deposited by any suitable method. Preferably, the platinum is deposited using an electroplating process and a suitable platinum source, such as a Pt P-salt with a formula of Pt(NH₃)₂(NO₂)₂ or Pt Q-salt with a formula of [Pt(NH₃)₄]HP0₄. However, due to the extra expense, using a platinum layer may not be cost effective in some modes of practice.

The surface 25 of body 11 optionally may be textured to enhance the bonding of layer 13 to body 11. The texture on surface 25 can be formed by a variety of techniques including molding the texture when body 11 is formed, embossing, chemical etching, sand blasting or otherwise abrading, laser ablation, combinations of these, and the like. When refurbishing components, sand blasting is a preferred technique to form the texture.

Thermal barrier structure 12 is provided on body 11. Thermal barrier structure 12 includes protective coating 13, a thermally grown oxide layer 14, and a ceramic topcoat 15. Protective coating 13 helps to protect body 11 against oxidation, particularly in high temperature environments (e.g., environments in which the temperature is above about 450°C, preferably above about 650°C, more preferably above about 850°C). In the practice of the present invention, protective coating 13 comprises at least one aluminide. As used herein, an aluminide refers to a metal compound comprising aluminum at and least one other more electropositive
metal element. In many forms, an aluminide is a metallic solid solution or an intermetallic composition. Examples of suitable aluminides include nickel aluminide, cobalt aluminide, combinations of these, and the like. The protective coating 13 may be a single phase or may include one or more additional phases.

Aluminide compositions comprising at least (a) aluminum and (b) nickel and/or Co are preferred. In the present invention, nickel aluminides and/or cobalt aluminides containing from about 45 to about 70 atomic percent Ni and/or Co based on the total amount of nickel, cobalt, and aluminum are preferred. Such compositions provide a good balance between high temperature oxidation resistance and acceptable mechanical properties.

One or more refractory elements also may be incorporated into all or a portion of the aluminide content of coating 13 if desired. As used herein, a refractory element refers to a metal element having a melting point greater than about 795°C, preferably greater than 1100°C, more preferably greater than 1850°C. Examples of suitable refractory elements include one or more of Hf, Zr, Y, La, Ce, rhenium, osmium, and combinations of these. Of these, hafnium (Hf), zirconium (Zr), yttrium (Y), lanthanum (La), cerium (Ce), and combinations of these are preferred. In more preferred embodiments, coating 13 comprises at least one of Hf, Zr, and/or Y, most preferably Hf. Advantageously, the refractory element content offers excellent oxidation protection by minimizing the amount of oxidized scale and enhancing the adherence of the scale to the protective coating system 12. The refractory elements may be present in coating 13 in a variety of forms including as metals, dopants, or non-metal compounds such as oxides, nitrides, carbides, combinations of these, or the like. These may be present in the same phase as other aluminide content or in separate phase(s).

The amount of refractory elements incorporated into coating 13 may vary over a wide range. If the content is too low, the content may not enhance oxidation resistance and/or adhesion as much as might be desired. If the content is too high, i.e. >15%, then oxidation resistance may not be further enhanced and may even be reduced. Balancing such concerns, coatings 13 may incorporate from 0.01 to 30 weight percent, preferably 0.1 to 20 weight percent, and more preferably 1 to 15
weight percent of refractory element(s) present in the surface of a coating as determined using SEM EDS spectroscopy techniques described below.

If a refractory element is present in coating 13 as an oxide, halide, nitride, carbide, salt, or other compound, e.g., HfO₂ or the like, the weight percent of refractory element in the coating is based on the amount of refractory element(s) that are present, not the compound(s) including the refractory element(s). For instance, if a particular coating includes 90 parts by weight of nickel aluminide and 10 parts by weight of HfO₂, the hafnium oxide content is 10% but the Hf content is 8.5% as determined by SEM EDS spectroscopy.

The weight percent of the refractory element(s) in the coating is based upon the total weight of all elements within the surface areas analyzed using SEM EDS techniques. In the practice of the present invention, a JEOL model 6610 scanning electron microscope equipped for energy dispersive spectroscopy (EDS) is used to determine the amount of refractory element(s) (such as hafnium) present in the surface of a coating, expressed as a weight percent. To determine such weight percents, 3 areas of a substrate are scanned at 20Kv, 50X magnification for 30 seconds from a working distance of 12 mm. The weight percent of each area is then determined from the SEM EDS data. The weight percent is taken as an average from the 3 areas. Scans may be taken on flat, concave, or convex areas such as the concave and convex airfoil as well as the buttress.

As coating 13 is formed (described in more detail below for an illustrative embodiment), a portion of the material that forms coating 13 tends to form an outward-growth coating portion 7 generally over the surface of body 11. Another portion of the material will tend to interdiffuse into and with the material of body 11, forming an interdiffusion zone 9 that extends to some depth into body 11. At the same time, some of the constituents of body 11 may diffuse into the deposited coating 13. For purposes of the present invention, interdiffusion zone 9 is considered to be a portion of the coating 13 even though it extends downward into body 11. Protective coatings 13 of the invention may include refractory element content within the outward growth portion 7 and/or the interdiffusion zone 9 of coating 13.
The coating 13 may have a thickness within a wide range. The thickness mentioned here is the total thickness of the outward growth portion 7 and the interdiffusion zone 9. In many embodiments, a suitable thickness for coating 13 is similar to the thickness of conventional industrial coatings, typically about 25 to 125 micrometers (about 0.001-0.005 inch).

Surface 27 of layer 13 optionally may be textured to enhance the adhesion of layer 13 to the oxide layer 14. The texture can be formed in a variety of ways. In some modes of practice, layer 13 is formed as a conformal coating over surface 25 so that the texture of surface 25 (if any) is telegraphed to some degree to surface 27 so that direct texturing of surface 27 after surface 27 is formed can be avoided. Such direct texturing creates a risk of abrading through layer 13, losing protection in those through-abraded regions. In other modes of practice, surface 27 can be texturized after surface 27 is initially formed if desired.

In illustrative modes of practice, protective coating 13 is formed using vapor phase coating techniques, including chemical (CVD) and/or physical (PVD) vapor deposition. For purposes of illustration, the process will be described in the context of preparing Hf-containing aluminide coatings in which Hf is obtained from one or more sources including an oxide, nitride, and/or carbide of Hf such as HfO2. It will be understood that coatings including one or more of the other refractory elements could be prepared by replacing all or a portion of the Hf sources described herein with comparable sources of one or more of the other refractory elements.

As an overview of one such process, at least one substrate including at least body 11 is placed into a processing chamber and suitably supported so that contact between the substrate and generated vapors causes the desired coating to form under suitable conditions. These conditions include carrying out the process at suitable temperatures in the presence of a reducing gas such as hydrogen. One suitable process chamber is described in WO 2010/135144, the entirety of which is incorporated herein by reference for all purposes. The supports on which substrates are supported desirably are pre-conditioned in order to enhance coating performance, e.g., improving the uniformity and consistency of the coating process. Pre-conditioning involves subjecting the supports to the coating process one or more times in the absence of any substrate(s). Optionally, the resultant aluminide
coating may be heat treated to adjust the coating microstructure and composition
distribution. Further background on using vapor phase coating techniques to form
aluminide coatings are described in WO 2010/135144, the entirety of which is
incorporated herein by reference for all purposes.

In more detail, the aluminide coatings of the present invention may be
obtained from ingredients comprising at least one aluminum source, at least one
non-halide compound of at least one refractory element, and a halide activator. These
ingredients may be supplied in any convenient form such as a fine powder, nuggets,
pellets, granules, flakes, or the like. These can be supplied in any convenient shape,
such as irregular, dendritic, acicular, cubic, spheroidal, fibrous, combinations of
these, and the like.

Aluminum used to form the aluminide content of coating may be derived
from a variety of sources. In one mode of practice, the aluminum is obtained from
commercially pure aluminum powder that may be mixed with an inert material such
as alumina for easier handling and to reduce the risk of sintering. In an exemplary
mode of practice, an aluminum source includes 1.5 to 10 parts by weight of
commercially pure aluminum powder per about 100 parts by weight of alumina.
The aluminum and alumina are powders of a size large enough to avoid undue
sintering while small enough to react well. In one mode of practice 200 mesh
aluminum powder and 100 mesh alumina would be suitable.

Other aluminum sources include any aluminum containing material(s)
suitable for use in physical or chemical vapor deposition in which an aluminum
containing vapor is generated from the source and caused to form coating on the
desired substrate. For example, other aluminum sources include Al-rich alloys
and/or intermetallic compositions optionally containing other elements such as those
other metals and refractory elements described herein with respect to forming
aluminide compositions. Examples include Cr, Co, Ni, Fe, Mo, W, Mn, Ti, Y, Zr,
Pt, Hf, combinations of these, or the like. The Al content in such sources desirably
is about 3 weight percent to about 99 weight percent, preferably from about 15
weight percent to about 50 weight percent based on the total weight of the source
material. The remainder of the source may be one or more of the other elements
described herein and/or compounds of such elements. An exemplary alloy source includes from about 25 weight percent to 35 weight percent aluminum.

In some modes of practice, aluminum incorporated into aluminum sources desirably is obtained from natural resources containing very little if any sulfur in order to exclude sulfur as much as practical from coating 13. Sulfur may tend to segregate to surfaces and could then adversely impact the oxide layer to base metal adhesion. In contrast, a superalloy such as the Mar M 247 alloy with less than 1 PPM bulk sulfur by weight tends to form a very adherent aluminum oxide just from the ~5.0% Al present for base material strength. Such a low sulfur alloy does not require the typical local enrichment of the component surface with aluminum using standard aluminide coating techniques. More preferred aluminum sources include sufficiently limited amounts of sulfur (if any) such that the resultant layer 13 includes less than 500 ppm, preferably less than 100 ppm, and even less than 10 ppm sulfur on a weight basis. Bauxite is a natural resource from which substantially sulfur-free aluminum can be obtained. Accordingly, aluminum sources derived from bauxite are preferred, particularly commercially pure aluminum powder.

Consequently, it also is desirable to minimize or avoid using aluminum donor materials which are alloyed with chromium. Chromium ores are largely sulfide type ores which often include substantial trace amounts of sulfur even after extensive refining. Aluminum donor materials containing chromium could include undue amounts of sulfur that could unduly contaminate the resultant aluminide coating. In many embodiments, therefore, it is preferred that chromium also is excluded from aluminum sources, and hence coating 13, as much as possible. Therefore, it is desirable that layer 13 includes less than 500 ppm, preferably less than 100 ppm, and even less than 10 ppm chromium on a weight basis.

When using a process chamber such as that described in PCT Patent Publication WO 2010/135144 (the entirety of which is incorporated herein by reference for all purposes), the amount of aluminum source materials desirably is about 0.3 kg to about 7 kg per cubic foot of the internal volume of the processing chamber, preferably from about 2 kg to about 4 kg per cubic foot of the internal volume of the chamber. This does not include diluent material, such as alumina, if included.
The additional metal elements (e.g., platinum, palladium, nickel, cobalt, titanium, chromium, silicon, combinations of these, and the like) used to form the aluminide(s) may be introduced from one or more sources including from substrate body 11, from the aluminum source(s), and/or from one or more independent source(s). Such elements may then react with the aluminum to form one or more aluminides. For example, as aluminum is deposited onto body 11 to form layer 13, one or more metallic constituents of body 11 such as Ni may diffuse or otherwise be incorporated into layer 13. The nickel and aluminum react to form nickel aluminide. From one perspective, such a process can be viewed as enriching the surface of body 11 to form an aluminum rich region constituted by layer 13.

The optional refractory element(s) may be provided by one or more sources wherein at least a portion of at least one source, preferably substantially all of the source, includes a non-halide compound of the element such as a salt, a metallic compound, an oxide, other oxygen-containing compound, nitride, carbide, and/or the like. Desirably, at least 25 weight percent, preferably at least about 50 weight percent, more preferably substantially all of the refractory element source(s) are such compound(s). Oxide sources are preferred. In an illustrative embodiment, a preferred Hf source is HfO₂. Advantageously, using an oxide of Hf as a source provides excellent control over the Hf activity when using vapor phase techniques for co-deposition of Hf and aluminum.

The refractory element source(s) optionally may include one or more halides of a refractory element if desired. Examples of such halides include chlorides and fluorides of one or more refractory elements, including HfCl₄, HfF₄, combinations of these, and the like.

In illustrative modes of practice, the amount of Hf source materials desirably is about 0.01 weight percent to about 10 weight percent, preferably about 0.05 weight percent to about 5 weight percent total amount of aluminum source materials, including diluent such as alumina, if any.

The halide activator includes one or more halide containing compounds including covalent compounds and salts. One function of the activator is to provide a chemical species which acts to help transfer the aluminum and/or hafnium from the source materials to the target. The activator typically has a sufficiently high
vapor pressure at typical coating temperatures that a reasonable reaction time can be achieved. Suitable halide activators include AlF₃, AlCl₃, NH₄F, NH₄Cl, NaF, NaCl, KF, KC1. Other activators include halide containing compounds such as CrF₂, one or more fluorinated polymers such as polytetrafluoroethylene (PTFE available from E. I. DuPont de Nemours under the trade designation TEFLOM), or the like. These preferably are present as a powder within the coating chamber. Vapor phase halides such as HF also may be introduced during the coating process.

AlF₃ is a preferred activator that is preferably used in amounts of about 0.4 to 2.4 moles per cubic foot of the internal volume of chamber 31, preferably of about 1.0 mole to about 1.5 moles per cubic foot of the internal volume of chamber 31. If other halide activators such as those noted are substituted for AlF₃, these would be used in amounts sufficient to achieve an equivalent level of activator activity. The activator materials are preferably supplied as fine powders having an average size less than 1 mm.

According to one methodology, constituents comprising the one or more aluminum sources, one or more halide activators are placed into the bottom of the processing chamber in trays. Desirably, these are pre-mixed powders. Then, one or more refractory element sources are provided as powders and sprinkled on top of the mixture. In one mode of practice, the aluminum source is obtained by mixing 5 parts by weight of commercially pure aluminum powder with 95 parts by weight of alumina. The aluminum source is pre-mixed with 3 to 10 parts by weight of AlF₃ per 100 parts by weight of aluminum powder and alumina. The refractory element source is 0.15 parts by weight of HfO₂ powder per 100 parts by weight of aluminum powder and alumina.

The substrate(s) to be coated are placed onto pre-conditioned supports such as a metal screen to that the substrates are out of contact with the solid coating materials during the coating process. The distance between the substrates and the solid coating materials can be changed to adjust the thickness of the resulting coatings. A typical distance is in the range from 9 cm to 20 cm. Optionally, the surface 25 of body 11 can be appropriately cleaned, activated, or otherwise treated. For instance, if body 11 is an original or replacement part, the surface can be cleaned. If body 11 is a used part that is being repaired, then a stripping process can
be used to remove previous coatings. Stripping can be followed by a suitable surface cleaning operation. The practice of the present invention removes at least some oxide from the surface(s) of body 11 during at least one incubation stage, as described below, and this helps to prepare body 11 as well.

A flow of an inert gas such as argon or nitrogen is initiated and used to purge air from the process chamber prior to heating. After the purge, the flow of inert gas is continued as the process chamber is heated to a temperature that is above the auto ignition temperature of hydrogen. In one mode of practice, the process chamber is heated to 1450 F under a flow of the inert gas. Once this temperature is reached, a flow of hydrogen and/or one or more other suitable reducing gases is introduced into the process chamber. The flow of the inert gas may be continued, reduced, or stopped. In one mode of practice, the flow of inert gas is stopped and a flow of substantially pure hydrogen is established.

The water content of the hydrogen tends to impact the refractory element content of the resultant coating. Generally, more refractory element is incorporated into the coating when the hydrogen is drier. In many modes of practice, dry hydrogen is used to obtain coatings with higher refractory element content.

After the flow of hydrogen and/or other reducing gas is established, the flow is maintained. The process chamber is further heated to increase the temperature as rapidly as practical to a temperature in the range from about 1700 F to about 1850F. The substrate(s) are then held in this temperature range for an extended period. The reason for doing this is that, in this temperature range, it is believed that equilibria tend to favor that the aluminum trifluoride reacts with hydrogen to form HF. HF is a strong oxide reducer that helps to remove residual oxides on the surface of the substrates. Mixtures of hydrogen and hydrogen fluoride have been used in the past to remove residual oxides and is referred to as in situ fluoride ion cleaning (FIC). However, it is believed that FIC has not been practiced to make aluminide coatings in the presence of nonhalide compounds of refractory elements such as Hf oxide.

At the same time, and without wishing to be bound by theory, it is believed that the HF (and/or other reaction product(s) of the halide activator and hydrogen) reacts with the hafnium oxide in a manner that significantly increases the amount of reactive Hf-containing species in the vapor phase to form the coatings. In practical
effect, incubation in this first heating stage occurs under conditions effective to form
one or more reaction products from one or more of the donor constituents in a
manner that favors more efficient incorporation of refractory elements into the
coating. Experiments have shown that carrying out this incubation in the presence
of hydrogen and the oxide significantly increases the Hf content of the resultant
coating than if the process were to be carried out in an inert gas or in a reducing gas
without incubation. Remarkably, coatings including 8 to 14 weight percent of Hf
based on the total weight of the coating can be made from donor materials that
include only 0.15 weight percent of Hf oxide based on the total weight of aluminum
and alumina sources.

In contrast, using a conventional approach without reducing gas and the
incubation yields coatings with only 0.35 weight percent Hf from donor sources
including 4.5 weight percent Hf oxide. The present invention uses less Hf content in
the sources and yet provides significantly more Hf in the coating by one to two
orders of magnitude! The present invention significantly improves the efficiency of
vapor phase deposition of hafnium and aluminum compared to what has been
accomplished previously.

It is also believed that the temperature regime used for the incubation
selectively favors oxide removal and formation of reactive Hf species relative to
coating formation. Indeed, during experiments, it is believed that little if any
aluminide coating formation occurs during the incubation phase at one or more
temperatures in the range from 1700°F to 1840°F.

The time period of the incubation in the temperature range from 1700°F to
1850°F occurs for a time period sufficient to remove at least a portion of the residual
oxide on the substrates and to prepare a vapor phase with an enhanced hafnium
reactivity content. In exemplary modes of practice, the incubation occurs for a time
period from 15 minutes to 5 hours, preferably 30 minutes to 5 hours, more
preferably 45 minutes to 5 hours, most preferably 1 hour to 3 hours. In one
experiment, holding the sample at 1775°F +/- 25°F for 90 minutes was suitable.

After the incubation, the process chamber is heated further to the desired
coating temperature(s). A suitable temperature is in the range from 1900°F to 2100
F. The process chamber is held at such temperature(s) for sufficient time to
produce a coating of the desired thickness. A suitable holding period for this stage is a time period in the range from 3 hours to 10 hours. In an exemplary experiment, the temperature was rapidly increased to 1975 F and then maintained at this temperature until the desired coating thickness was established. Although the coating reaction proceeds at a suitable rate during this stage, it is believed that the reaction to produce additional reactive Hf species may still be occurring. The weight percent of refractory elements) incorporated into the coating (based on the total weight of the coating) is greater than the weight percent of the refractory element constituents included in the constituent donor materials (based on the total weight of the aluminum sources).

To stop the coating reaction, both heating and the flow of hydrogen gas is stopped and the process chamber is flushed with a flow of inert gas such as argon. The process chamber is cooled under the inert flow to room temperature.

Referring again to Fig. 1, thermally grown oxide (TGO) layer 14 is provided on protective layer 13. Desirably, the protective coating 13 is sufficiently rich in Al to form a layer 14 that is a protective oxide (TGO) scale of α-Al2O3. The scale may be grown by any suitable oxidizing technique including growing the oxide thermally in an atmosphere including one or more oxidizing agents, chemically oxidizing the coating 13 via application of an oxidizing liquid, combinations of these, and the like.

In addition to imparting oxidation resistance, the oxide layer 14 helps bond the ceramic topcoat 15 to the protective coating 13.

Layer 14 is formed by oxidizing layer 13 under conditions to form an oxide scale comprising aluminum oxide. Under conventional practices, a thermally grown oxide forms between a bond coat and a ceramic coat when the surface of the bond coat oxidizes. Conventionally, a portion of the thermally grown oxide may grow in situ as the ceramic layer is formed. In other practices, the thermally grown oxide layer forms in situ between the formed bond coat and ceramic coating when the component bearing the bond and ceramic coatings is used in a high temperature environment in which an oxidizing agent is present.

In contrast, in the practice of the present invention, at least a majority of, preferably substantially all of, the thermally grown oxide layer 14 is formed in situ on protective layer 13 before the ceramic topcoat layer 15 is formed. In this way,
thermal barrier structure 12 is essentially fully formed before structure 12 is exposed to temperature cycling so that the displacement and stress effects caused by TGO growth between already existing bond coat and ceramic layers is avoided. Adhesion among the layers 13, 14, and 15 as well as between structure 12 and body 11 is substantially improved.

The thermally grown oxide layer 14 can be formed in a variety of ways. According to one mode of practice, the protective layer 13 is formed on body 11. Then, before the ceramic topcoat is formed, the coated body 11 is placed into a furnace and heated under conditions effective to oxidize the layer 13 to form oxide coating 14. Aluminum oxide forms. Other metals present in layer 13 might also form oxides. The aluminum oxide is formed to a point of oxide saturation after which little or no additional aluminum oxide forms. At this stage, the surface of layer 13 is generally fully oxidized with an oxide coating that forms an impermeable barrier protecting the remainder of layer 13 as well as body 11 against further oxidation.

A variety of conditions may be used to form the oxide layer 14. The oxide generally is formed in the presence of an oxidizing agent. Oxygen in the ambient air is one suitable oxidizing agent. Other oxidizing agents include ozone, peroxide, combinations of these, and the like. An air furnace is an exemplary processing chamber useful for forming the oxide layer 14. The temperature used to form the oxide may be selected from a wide range of temperatures. In some modes of practice, using a temperature in the range from about 900 F to about 1500 F, preferably 1200 F to about 1500 F, more preferably 1300 F to 1400 F would be suitable. The processing time may occur over a wide range of time periods.

Desirably, the processing time occurs for a time period sufficient to fully oxidize the surface of layer 13. More desirably, the processing time occurs for a time period sufficient to reach a point of oxide saturation such that further processing yields little if any additional oxide growth. In some modes of practice, a time period from 2 minutes to 8 hours, preferably 5 minutes to 4 hours, more preferably from about 30 minutes to 2 hours, even more preferably about one hour would be suitable.

Surface 29 of layer 14 is textured to enhance the adhesion of layer 14 to the ceramic layer 15. The texture can be formed in a variety of ways. In some modes of
practice, layer 14 is formed as a conformal coating over surface 27 so that the
texture of surface 27 is telegraphed to some degree to surface 29. This allows direct
texturizing of surface 29 after surface 29 is formed can be avoided. Such direct
texturizing creates a risk of abrading through layer 14, losing protection in those
through-abraded regions. In other modes of practice, surface 29 can be texturized
after surface 29 is initially formed if desired.

Ceramic topcoat 15 helps to extend the service life of article 10 at least in
part by reducing the surface temperature at the surface 17 of thermally grown oxide
layer 14 relative to the surface 18 of the topcoat 15. In practice, it is believed that
the temperature differential between surfaces 17 and 18 is above 100°C.

The ceramic topcoat 15 can be formed from a wide variety of ceramic
materials. Suitable ceramic materials have one or more of low thermal conductivity,
high oxygen permeability, and a relatively high coefficient of thermal expansion. In
a representative embodiment, the topcoat 15 includes yttria-stabilized zirconia (YSZ) that contains about 2 to about 12 weight percent, preferably about 4 to about
8 weight percent yttrium oxide.

The topcoat 15 can be formed in a variety of ways. In some embodiments, the topcoat may be applied either by plasma spraying or electron beam physical
vapor deposition. Plasma spraying techniques, e.g., air plasma spraying, are
preferred. In many embodiments, the topcoat has a thickness of about 100 microns
to 400 microns. Because oxide layer 14 is substantially formed prior to formation of
ceramic topcoat 15, ceramic topcoat can be formed in a wide variety of conditions,
including under ambient conditions. In other modes of practice, ceramic topcoat 15
is formed in a protected environment comprising an inert gas and/or a reducing gas.

The principles of the present invention will now be described with respect to
the following illustrative examples.

**Example 1**

**Aluminiide coated vane segments**

Several first stage vane segments of a Rolls Royce 501K engine was
removed for evaluation and replacement of the thermal barrier coating (TBC). The
501K engine is a variant of a 4000 SHP gas turbine developed for aircraft propulsion in the mid 1950's known as the T56. The current version of the T56, the T56-A-15,
utilizes many of the same components as the 50IK. While the T56 is a flight engine which experiences relatively frequent cycling, the version of the 50IK engine of interest is used for power generation. With a conventional thermal barrier coating (TBC) system on the first stage vanes, the engine operates approximately 18,000 hours running 24/7 with a shutdown for inspection about every 4 months or 2500 hours of running time. A current limitation to time between overhauls is adherence of the thermal barrier coating on the first stage vane segments.

Analysis of the vane segments showed that the coating system was an EBPVD type zirconia ceramic on a platinum aluminide bond coat applied to both X40 and Marm247 vane segments. The aluminide coating was present on both the external and internal surfaces of the vane segment with platinum present only on the gas path of the part.

Based on the type of application, the use of the highly strain compliant EBPVD type ceramic does not appear necessary given the roughly 2500 hour duration cycle. In fact, it would appear that based on cost and intended usage, an air plasma sprayed ceramic coating would be more cost effective and protect the substrate more effectively due to the lower thermal conductivity of the plasma sprayed versus EBPVD structure.

To evaluate the potential of use of the plasma sprayed structure versus the EBPVD zirconia, a vapor phase coating process to coat the internal and external surfaces of the 501K first stage vane was used to coat the vane segment with an aluminide coating. The aluminide coated vane segments were then used in the experiments described below in Examples 2, 3, and 4. A group of test parts was coated targeting about 2.5 to 3.0 mils of aluminide coating with a basic chemistry similar to current industry standards except in this case there was no precoat platinum additions via electroplating.

**Example 2**

**Applying ceramic coating directly to grit blasted aluminide coating**

Aluminide coated vanes from Example 1 were used. The surfaces of the vanes were grit blasted to improve adherence of the plasma sprayed zirconia using 24 grit SiC at 15 PSI. One purpose of the roughening is to provide a mechanical
lock for the zirconia. Grit blasting the aluminide coating is a standard procedure for preparation of the surface for the ceramic coating. Compared to a normal superalloy surface, the aluminide coating applied as a bondcoat is much more brittle and very thin. Therefore, special care was taken to roughen the aluminide surface sufficiently for the zirconia to adhere without completely removing the aluminide bond coat. An industry standard yttria stabilized zirconia coating was then applied to the surface of the vane segment using a robot.

The quality of the ceramic coating was assessed visually. The ceramic coating adhered to the aluminide in certain areas of the part but visually flaked in others.

Additionally, a vane segment was metallurgically sectioned through the airfoil using a diamond saw and then mounted to examine the coating microstructure. Visual examination of the cut edge of the airfoil showed areas where the ceramic coating had adhered when cut in compression. However, in areas where the ceramic coating was in tension, the ceramic coating was substantially chipped off of the vane. Metallurgical examination of the coating microstructure showed the aluminide bond coat to be thin and varying in thickness due to the grit blasting with the 24 grit SiC. Adherence between the aluminide bond coat and ceramic coating was not continuous and correlated with the visual appearance of the vane segment.

**Example 3**

**Applying aluminide and ceramic coatings to grit blasted vane segment**

To avoid thinning the aluminide bond coat by grit blasting with SiC prior to application of the ceramic and yet still get the roughened surface desirable for the ceramic to adhere, vane components were prepared differently than in Examples 1 and 2. Prior to aluminide coating, vane samples were grit blasted with 24 grit SiC at 15 PSI to produce a roughened surface. The aluminide coating was then applied to both the internal and external surfaces of the vanes as described in Example 2, except that the aluminide coatings were not grit blasted.

The visual appearances of the external surfaces of the aluminide coated vanes showed a rougher surface than the grit-blasted aluminide surfaces of Example
2, although the aluminide coatings of the present example were not as rough as the grit blasted vane surfaces prior to aluminide coating. The aluminide coating followed the contours of the vane surface. This smoothed the high peaks, but the aluminide coating did not fill in the surfaces irregularities.

Using the same process as Example 2, the same yttria stabilized zirconia was coated onto the aluminide coated vane samples. Visually, the ceramic coating adhered to more areas of the part than in Example 1. This was attributed to the fact that the vane samples could be grit blasted more aggressively since grit blasting was done before aluminide coating. This avoided the concern that the aluminide coating would be blasted off if the grit blasting were practiced too aggressively after aluminide coating. Optionally, the aluminide coatings could be lightly grit blasted or otherwise textured after aluminide coating if desired.

The coated vane segments were sectioned through the airfoils with a diamond saw. The chipping on both the tension and compression sides was reduced relative to Example 2 but not eliminated. Metallurgical examination of the coating system microstructure showed the bond coat to be uniform and adequate in thickness. Examination of the interface layer between the oxide layer and the ceramic top coat showed non uniform adherence, however.

**Example 4**

**Applying aluminide coating, growing thermal oxide, and then applying ceramic coatings to grit blasted vane segment**

Based on knowledge of EBPVD applied ceramic thermal barrier coatings, it was known that between the bond coat and the ceramic top coat, an oxide layer forms on the bond coat during engine operation. If the oxide layer forms after the ceramic layer has been applied or during ceramic layer formation, the growth of the oxide layer introduces a strain which can impair the service life of the coating system. To avoid this, an oxide layer is deliberately thermally grown in the present example to the point of oxide saturation prior to applying the ceramic coating. That is, the oxide grows up to a certain point and then substantially stops growing even with further processing. This point of maximum oxide formation is the point of oxide saturation.
Further, because the aluminide surfaces of Example 3 were already roughened to improve the mechanical adherence, it was proposed to evaluate a coating system using a thermally grown oxide on the roughened, aluminide bond coat surface prior to applying a plasma sprayed yttria stabilized zirconia. This was done because the oxide layer would form subsequently anyway, and it was theorized that an oxide to oxide adhesion would be better than metal to oxide adhesion if the strain effects could be reduced or avoided.

To test this theory, test vanes were grit blasted and aluminide coated in accordance with Example 3. Following aluminide coating, the parts were heat treated in an air circulating furnace to deliberately create an oxide coating that would form during engine operation between the bond coat and the ceramic coat. Temperatures of 1125F, 1300F, 1350F and HOOF were used to deliberately form the oxide layer on vane segments, respectively. The color of the oxide formed depending on the temperature. The oxide conditions allowed the oxide to grow to the point of oxide saturation.

Following oxidation, the vane segments were plasma sprayed to form a ceramic coating on the thermally grown oxide in accordance with Examples 2 and 3. Visually, the ceramic coating was continuously formed and there was no evidence of adherence issues on the samples oxidized at the higher temperatures from 1300F to HOOF anywhere on the parts. The vane segments were cut with a diamond saw exposing the coating to both compressive and tensile loads. No chipping was observed on any tension edges. Even when cut in tension, the coatings showed almost no chipping.

Metallurgical examination of the airfoil sections showed the following:

- The aluminide bond coat showed adequate thickness in all areas of .0022" to .0025".
- The thickness and distribution of the ceramic topcoat was within typical thicknesses for this application.
- There was a thin, thermally grown oxide present between the bond coat and the ceramic top coat over the entire surface of the vane segment.
- The adherence between the aluminide bondcoat and ceramic top coat was exceptional and uniform over the whole part. The test parts
oxidized at 1350F and 1400F had the best adherence evaluated metallurgically.

**Example 5**

Applying aluminide coating, growing thermal oxide, and then applying ceramic coatings to grit blasted vane segment

The process of Example 4 was repeated multiple times using vane samples in which the thermally grown oxide resulted from oxidation at both 1350 F and 1400 F. Multiple sections were taken with the diamond saw to verify the eddy current thickness readings with actual thicknesses. Visual evaluation of the coating adherence was excellent and consistent across all samples. Metallurgical inspection of the coating adherence between the bond coat and ceramic top coat validated the excellent visual adherence.

Further confirmation of the adherence of the thermal barrier coating system is provided by the fact that the removal of the zirconia layer was performed to reuse samples which were not destructively evaluated. This was done by grit blasting the coated vanes using aluminum oxide at a variety of pressures. As the process was modified from Example 2 through Example 4, it became more difficult and time consuming to prepare parts for future trials.

**Example 6**

Several aluminide coatings were formed on cleaned superalloy substrates. The substrates included Co-based and Ni-based superalloys. In each experiment, the aluminum source included 5 lbs of aluminum powder mixed with 95 lbs of alumina powder. This was mixed with 10 weight percent of A1F₃ based on the total weight of the aluminum source. The mixture was placed into a process chamber in trays. Depending upon the run, 0.15 to 0.50 weight percent of HfO₂ powder was sprinkled on top of the mixture. The percentage of the hafnium oxide was based on the total weight of the aluminum source and the A1F₃. The substrate was placed into the process chamber and supported on a pre-conditioned mesh above the donor materials.

The process chamber was purged with argon. Maintaining the flow of argon, the temperature in the process chamber was increased to 1450 F. At this point, a flow of hydrogen was established and maintained while the flow of argon stopped.
The temperature was then further increased to 1750°F. At this stage, the temperature ramp rate was substantially reduced so that the sample incubated at 1775°F +/- 25°F for 90 minutes. In accordance with principles of the present invention, it is believed that a substantial portion of the hafma was reduced to one or more reduced species during this time period in this temperature range.

After this first stage of incubation, heating continued up to 1975°F for the samples having Ni-based alloy substrates and up to 2000°F for the samples having Co-based alloy substrates. At that point the process chamber was maintained at 1975°F or 2000°F under a flow of hydrogen for about 6 hours (Ni-based alloy substrates) or about 15 hours (Co-based alloy substrates) to complete the formation of the coating on the substrate. After this, heating and the flow of hydrogen was stopped, and a flow of argon was established to purge the chamber. The chamber contents were cooled to room temperature under the flow of argon. This temperature is suitable when the substrate includes a nickel-based superalloy. For a substrate including a Co-based superalloy, coating temperatures approximately 25°F higher would be more suitable.

Metallurgical evaluation showed the hafnium to exist as discrete particles of hafnium containing compound(s). The benefits of hafnium additions of this type to improve the oxidation resistance are well established.

The aluminum and hafnium contents of each sample were measured using SEM EDS. The results are shown in the following table.
<table>
<thead>
<tr>
<th>Run no.</th>
<th>Material</th>
<th>Rejuvenation Data</th>
<th>T-t cycle, Flows</th>
<th>Test Results, AVE. Coating Thk (inches)</th>
<th>Results, EDS Surface %AI by EDS Surface %Hf by EDS</th>
<th>Oxidation Test Cycle, T-t decay</th>
<th>Oxidation Test Results, Qualitative Comments, Metallochronic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X-40, Co base</td>
<td>10.0% AlF3 5.0% Al 0.15% Hf</td>
<td>2000F+/−25F-24 hrs, H2 atm Then: Flows: 80cfh H2</td>
<td>0.0023&quot;</td>
<td>27.5% Al 5.4% Hf</td>
<td>2050F-47 hr 1120C-47 hr</td>
<td>Excellent; No spikes no growth</td>
</tr>
<tr>
<td>2</td>
<td>Mar-m-247, Ni base</td>
<td>10.0% AlF3 5.0% Al 0.15% Hf</td>
<td>1975F+/−25F−12 hrs, H2 atm Then: 1975F+/−25F-3 hrs in Argon Flows: 56 cfh Argon and H2</td>
<td>0.0075&quot;</td>
<td>28.2% Al 10.8% Hf</td>
<td>2050F-47 hr 1120C-47 hr</td>
<td>Excellent; Very little growth; No spikes</td>
</tr>
<tr>
<td>3</td>
<td>X-40, Co base</td>
<td>10.0% AlF3 5.0% Al 0.15% Hf</td>
<td>2000F+/−25F-24 hrs, H2 atm Then: 2000F+/−25F-3 hrs in Argon Flows: 80 cfh Argon and H2</td>
<td>0.0028</td>
<td>25.4% Al 14.0% Hf</td>
<td>2050F-47 hr 1120C-47 hr</td>
<td>Excellent; Very little growth; No spikes</td>
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<tr>
<td>4</td>
<td>Mar-m-247, Ni base</td>
<td>5.0% AlF3 2.5% Al 0.275% Hf02</td>
<td>1975F+/−25F-6 hrs, H2 atm Then: 1975F+/−25F-2</td>
<td>0.0050</td>
<td>32% Al 6.7% Hf</td>
<td>2050F-47 hr 1120C-47 hr</td>
<td>Excellent; Very little growth; No spikes</td>
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<td>5</td>
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<td>85.0 lb basis</td>
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<td>hrs in Argon Flows: 70 ecfh Argon and H2</td>
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<td></td>
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<td>2000F+/-25F-32 hrs, H2 atm</td>
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<td>Then: 2000F+/-25F-8 hrs in Argon Flows: 80 ecfh Argon and H2</td>
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<tr>
<td>6</td>
<td>Mar-m-247, Ni Base</td>
<td>3.0% A1F3, 1.5% Al, 0.10% HIO2</td>
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<td>57.6 lb basis</td>
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<tr>
<td></td>
<td></td>
<td>hrs in Argon Flows: 50 ecfh Argon and H2</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.0040&quot; (too thick)</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>32% Al, 8.2% Hf</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Excellent; Some growth; No spikes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>X-40</td>
<td>7.5% A1F3, 3.75% Al, 0.15% HF02</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>60.8 lb basis</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>hrs in Argon Flows: 56 ecfh Argon and H2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.0028&quot; OXIDATION IN COATING</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>33% Al, &lt;2% Hf</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Excellent; Some growth; No spikes but underlying oxidation probably arising from original bond coat issues</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>8</td>
<td>X-40</td>
<td>7.5% AlF3</td>
<td>3.75% Al</td>
<td>0.17% HfO2</td>
<td>60.0 lb basis</td>
<td>2000F+/-.25F-21 hrs, H2 atm</td>
<td>Then: 2000F+/-.25F-4 hrs in Argon</td>
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</tr>
<tr>
<td>9</td>
<td>X-40</td>
<td>7.5% AlF3</td>
<td>3.75% Al</td>
<td>0.17% HfO2</td>
<td>56.8 lb basis</td>
<td>2000F+/-.25F-17.5 hrs, H2 atm</td>
<td>Then: 2000F+/-.25F-4.5 hrs in Argon</td>
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<td>10</td>
<td>X-40</td>
<td>7.5% AlF3</td>
<td>3.75% Al</td>
<td>0.17% HfO2</td>
<td>57.6 lb basis</td>
<td>2000F+/-.25F-18 hrs, H2 atm</td>
<td>Then: 2000F+/-.25F-3 hrs in Argon, Incoming 112 dew point issue</td>
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</table>
Note that the weight percent $\text{AIF}_3$ is based on the total weight of the aluminum source. The weight percent of the $\text{HfO}_2$ based on the total weight of the aluminum source and $\text{AIF}_3$. 
Remarkably, hafnium contents in the range from 5 to 39.9 weight percent were achieved using donor materials that included no more than 0.50 weight percent of hafnium oxide. Whereas conventional vapor phase coating strategies selectively favor aluminum over Hf deposition even when using higher amounts of Hf donor materials are used, the present invention in practical effect reverses this co-deposition selectivity to transfer the Hf consistently and efficiently when co-deposited with aluminum.

Oxidation resistance at high temperature also was assessed qualitatively. It is known that Hf facilitates oxidation resistance up to a certain level of incorporation. Beyond a certain level, it is known that additional amounts of Hf content may not help oxidation resistance and may even lower it. This was in fact observed. Samples including 5.4 to 14.2 weight percent Hf showed good and excellent levels of oxidation resistance. The samples including 29 and 39.9 weight percent Hf showed fair oxidation resistance. Although the present invention allows such high Hf content to be achieved using very little Hf in the donor materials, using so much Hf might not be suitable when high temperature oxidation resistance is desired.

A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.
WHAT IS CLAIMED IS:

1. A method of forming a thermal barrier coating comprising:
   (a) providing a substrate comprising at least one metallic surface;
   (b) roughening at least a portion of the metallic surface
   (c) forming a coating on at least a portion of the roughened surface of the substrate, wherein the coating comprises at least one aluminide; and
   (d) treating the aluminide coating under conditions effective to form an oxide coating on the aluminide coating;
   (e) after forming the oxide coating, forming a third coating on the oxide coating, said third coating comprising at least one ceramic material.

2. The method of claim 1, wherein step (c) comprises forming an aluminide coating comprising a refractory element.

3. The method of claim 2, wherein the refractory element is Hf.

4. The method of claim 1, wherein step (a) comprises providing a coating comprising platinum on the substrate surface.

5. The method of claim 1, wherein step (c) comprises using a vapor phase to form the coating comprising the at least one aluminide.

6. The method of claim 1, wherein the aluminide comprises platinum.

7. The method of claim 1, wherein the substrate comprises a Ni-based alloy.

8. The method of claim 1, wherein the substrate comprises a Co-based alloy.

9. The method of claim 1, wherein the substrate comprises an alloy comprising Ni and Fe.

10. The method of claim 1, wherein step (b) comprises roughening at least a portion of the metallic surface with at least one of sanding or grinding.
10. The method of claim 1, wherein step (a) occurs in the presence of an activator.

11. The method of claim 10, wherein the activator comprises A1F₃.

12. The method of claim 10 or 11, wherein step (c) comprises the steps of:
   (i) providing an aluminum source, a refractory element source, and the activator in a process chamber;
   (ii) introducing a flow of hydrogen into the process chamber;
   (iii) increasing the temperature of the process chamber to a temperature in the range of 1700 F to 1850 F and holding the temperature in this range for a time period in the range from 15 minutes to 5 hours; and
   (iv) in the presence of hydrogen, maintaining the process chamber in a temperature range from 1900 F to 2100 F for a time period in the range from 3 hours to 10 hours.

13. The method of claim 10 or 11, wherein step (c) comprises the steps of:
   (i) providing an aluminum source, a refractory element source, and the activator in a process chamber;
   (ii) introducing a flow of hydrogen into the process chamber;
   (iii) in the presence of hydrogen, holding the process chamber in a temperature range from 1700 F to 1850F; and
   (iv) in the presence of hydrogen, holding the process chamber in a temperature range from 1900 F to 2100F.

14. The method of claim 1, wherein step (c) comprises providing an oxide of hafnium.

15. The method of claim 1, wherein step (c) comprises providing an aluminum source, wherein the aluminum source comprises less than 500 ppm sulfur on a weight basis.
16. The method of claim 1, wherein step (c) comprises providing an aluminum source, wherein the aluminum source comprises less than 500 ppm chromium on a weight basis.

17. The method of claim 1, wherein step (c) comprises providing an aluminum source, wherein the aluminum source comprises aluminum powder and alumina.

18. The method of claim 1, wherein step (d) comprises heating the coating comprising at least one aluminide in the presence of ambient air.

19. The method of claim 1, wherein step (d) comprises heating the coating comprising at least one aluminide in the presence of ozone.

20. A method of refurbishing a coated article comprising:

(a) providing an article having a metallic surface and a coating on at least a portion of the metallic surface;

(b) treating the article under conditions effective to remove at least a portion of the coating from the metallic surface, wherein said treatment roughens at least a portion of the metallic surface from which the coating is removed;

(c) forming a coating on at least a portion of the roughened surface, said coating comprising at least one aluminide;

(d) treating the aluminide coating under conditions effective to form an oxide coating on the aluminide coating;

(e) after forming the oxide coating, forming a third coating on the oxide coating, said third coating comprising at least one ceramic material.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/051883

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C23C 10/48 (2014.01)
CPC - C23C 10/48 (2014.09)

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)
IPC(8) - C23C 10/04, 10/06, 10/08, 10/10, 10/12, 10/14, 10/16, 10/48, 10/50, 16/12 (2014.01)
CPC - C23C 10/04, 10/06, 10/08, 10/10, 10/12, 10/14, 10/16, 10/48, 10/50, 16/12 (2014.09)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 427/250, 252, 253

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>US 6,103,386 A (RAYBOULD et al) 15 August 2000 (15.08.2000) entire document</td>
<td>1-19</td>
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<td>Y</td>
<td>US 5,656,614 A (BASTA et al) 19 August 1997 (19.08.1997) entire document</td>
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<td>A</td>
<td>US 4,321,311 A (STRANGMAN) 23 March 1982 (23.03.1982) entire document</td>
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</table>

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed
  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search
09 October 2014

Date of mailing of the international search report
2 - 0 NOV 2014

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PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)