METHOD FOR FORMING A THERMAL BARRIER COATING

BACKGROUND OF THE INVENTION

The technology disclosed herein relates generally to coatings of the type used to protect components exposed to high temperature environments, such as the hostile thermal environment of a gas turbine engine.

Environmental coatings and thermal barrier coating (TBC) systems are applied to the external surfaces of components to protect them from oxidizing and corrosive environments. Additionally, the ceramic insulating layer of the TBC systems increases the efficiency of the engine by increasing surface temperatures of blades and vanes.

To be effective, thermal barrier coatings must have low thermal conductivity, strongly adhere to the component, and remain adherent throughout many heating and cooling cycles. The latter requirement is particularly demanding due to the different coefficients of thermal expansion between materials having low thermal conductivity and superalloy materials typically used to form turbine engine components. TBC systems capable of satisfying the above requirements have generally required a bond coat, such as diffusion coatings (i.e., diffusion aluminides and platinum aluminides) and overlay coatings (i.e., MCrAlX, where M is iron, cobalt and/or nickel and X is yttrium or other rare earth element). Ceramic layers formed of metal oxides such as zirconia that is partially or fully stabilized by yttria, magnesia, or other oxides, have been widely employed as materials for thermal barrier coatings. The ceramic layer is typically deposited by air plasma spraying (APS), low pressure plasma spraying (LPPS), or a physical vapor deposition (PVD) technique, such as electron beam physical vapor deposition (EBPVD), which yields a strain-tolerant columnar grain structure.

The aluminum content of the above-noted bond coat materials provides for the slow growth of a strong adherent continuous aluminum oxide layer (alumina scale) at elevated temperatures. This thermally grown oxide (TGO) protects the bond coat from oxidation and hot corrosion, and chemically bonds the ceramic layer to the bond

coat. However, a thermal expansion mismatch exists between the metallic bond coat, alumina scale, and ceramic layer. Tensile stresses generated by this mismatch gradually increase over time to the point where spallation can occur at the interface between the bond coat and alumina scale or the interface between the alumina scale and ceramic layer. Furthermore, although bond coat materials are particularly alloyed to be oxidation-resistant, the surface oxidation and interdiffusion (with the substrate) that occurs over time at elevated temperatures gradually depletes aluminum from the bond coat. Eventually, the level of aluminum within the bond coat can become sufficiently depleted to prevent further slow growth of the protective alumina scale and to allow for the more rapid growth of nonprotective oxides, the result of which again is spallation of the ceramic layer.

At lower process temperatures (i.e., about 1600 to about 2000 °F, about 871 to about 1093 °C), the alumina scale includes predominately meta-stable alumina (gamma- and theta-) with little or no alpha-alumina. Prior to deposition of the ceramic layer, the bond-coated article is usually preheated to about 1700 to about 1900 °F (about 927 to about 1038 °C). This preheat process is also not favorable to alpha-alumina formation. The meta-stable alumina phases transform to the more stable alpha-alumina over time. However, undesirable volumetric changes accompany the transformation between alumina phases. Additionally, the meta-stable phases generally exhibit high growth rate, poor adherence, and intrinsic porosity.

From the above, it is apparent that the service life of a TBC system is dependent on the bond coat used to anchor the thermal insulating ceramic layer. Consequently, considerable effort is directed to improved bond coats for TBC systems.

For example, bond coats formed of an overlay (i.e., not diffusion) of predominantly beta (β) phase nickel aluminide (NiAl) intermetallic have been proposed for use in high temperature applications. Additionally, overlay environmental coatings and bond coats comprising predominantly gamma prime-phase nickel aluminide (Ni_3Al) are under investigation.

Improvement in performance of the coating system is a continuing requirement in order for components to survive the increasingly severe operating conditions in high

performance gas turbine engines. Therefore, it is desirable to provide coating systems and methods for enhancing performance, particularly at the interface between the bond coat and the ceramic layer.

BRIEF DESCRIPTION OF THE INVENTION

The above-mentioned need or needs may be met by exemplary embodiments which provide methods for coating articles. The disclosed methods provide coatings having increased oxidation resistance and reduced spallation of the ceramic layer, if present, by promoting formation of stable α-alumina scale on a protective overlay coating.

In one exemplary embodiment, a method includes providing a coated superalloy substrate having an overlay coating on at least one surface, and subjecting the coated substrate to predetermined conditions to grow an aluminum oxide scale on the overlay coating, wherein the aluminum oxide comprises predominantly alpha phase alumina. The overlay coating is selected from the group consisting of a nickel aluminide intermetallic predominantly of beta phase, a nickel aluminide intermetallic predominantly of beta plus gamma prime phases, a nickel aluminide intermetallic predominantly of gamma plus gamma prime phases, and a nickel aluminide intermetallic predominantly of gamma prime phase.

In another exemplary embodiment, a method includes providing a coated superalloy substrate with an overlay coating on at least one surface. The overlay coating is selected from the group consisting of a nickel aluminide intermetallic predominantly of beta phase, a nickel aluminide intermetallic predominantly of beta plus gamma prime phases, a nickel aluminide intermetallic predominantly of gamma plus gamma prime phases, and a nickel aluminide intermetallic predominantly of gamma prime phase. The selected overlay coating is physically modified by milling, honing, or grit blasting. The coated substrate is heated in a vacuum chamber at a temperature of at least about 2000 °F (1093 °C) to about 2100 °F (1149 °C), for at least about 2 to about 8 hours, under a vacuum of from 10^{-3} to about 10^{-6} Torr to grow a predominantly alpha phase aluminum oxide scale on the selected overlay coating. The coated substrate is then pre-heated in a deposition chamber at a temperature of from about

1700 °F (927 °C) to about 2000 °F (1093 °C) for about 10 to about 30 minutes. Finally, a thermally insulating ceramic layer is deposited on the overlay coating.

BRIEF DESCRIPTION OF THE DRAWINGS

The subject matter which is regarded as the invention is particularly pointed out and distinctly claimed in the concluding part of the specification. Exemplary embodiments may be best understood by reference to the following description taken in conjunction with the accompanying drawing figures in which:

FIG. 1 is a perspective view of a turbine blade;

FIG. 2 is an enlarged schematic sectional view through the turbine blade of FIG. 1, taken on the line 2-2, showing a thermal barrier coating system on the blade.

FIG. 3 is a graph showing the results of Furnace Cycle Testing.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings wherein identical reference numerals denote the same elements throughout the various views, FIG. 1 shows an exemplary component, such as a turbine blade 10, that is operable within environments characterized by relatively high temperatures, and are therefore subjected to severe thermal stresses and thermal cycling. Other exemplary components include, but are not limited to, turbine nozzles and blades, shrouds, combustor liners, and augmentor hardware of gas turbine engines.

The blade 10 generally includes an airfoil 12 against which hot combustion gases are directed during operation of the gas turbine engine, and whose surface is therefore subjected to severe attack by oxidation, corrosion, and erosion. The exemplary airfoil 12 is anchored to a turbine disk (not shown) with a dovetail 14 formed on a root section 16 [looks like it points to the platform and not the whole of the root section] of the blade 10. Cooling passages 18 may be present in the airfoil 12 through which bleed air is forced to transfer heart from the blade 10. While reference is made herein to a particular component, i.e., blade 10, the teachings herein are generally applicable

to any component on which an environmental or thermal barrier coating system may be used to protect the component from its environment.

Represented in FIG. 2 is an exemplary thermal barrier coating system 20 illustrated as a longitudinal section through airfoil 12, which serves as substrate 22. As shown, the exemplary coating system 20 includes a protective layer 24, which overlies at least a surface of substrate 22. Optionally, as shown in the figure, a ceramic layer 26 overlies and contacts [your figure shows a TGO layer 28 that will exist between the 24 and 26. Are you concern this may be viewed as "separating" 24 from 26 and therefore they would not be in contact?] the protective layer 24. When there is no ceramic layer 26 present, the protective layer 24 is termed an "environmental coating." When there is a ceramic layer 26 present, the protective layer 24 is termed a "bond coat."

In an exemplary embodiment, deposition of the protective layer 24 may result in virtually no diffusion between the overlay coating and substrate 22. During subsequent processing, a thin diffusion zone 30 may develop. A minimal thickness of the diffusion zone in the overlay coating reduces the amount of substrate material that must be removed during refurbishment of the coating system 20, as compared to a diffusion-type bond coat.

The substrate 22 is preferably a high-temperature material, such as an iron, nickel, or cobalt-base superalloy. Exemplary materials include Rene N4, Rene N5, Rene N6. These superalloys are presented as examples, and the teachings disclosed herein are not limited for use with substrates of these materials.

The ceramic layer 26 may be an yttria-stabilized zirconia (YSZ), which may be about 6 to about 8 weight percent yttria, although other ceramic materials could be used, such as yttria, non-stabilized zirconia, or zirconia stabilized by ceria (CeO_2), magnesia (MgO), scandia (Sc_2O_3), or other oxides. The ceramic layer 26 is deposited to a thickness that is sufficient to provide the required thermal protection for the underlying substrate 22, generally on the order of about 125 to about 300 micrometers. The ceramic layer 26 may be deposited by physical vapor deposition (PVD) to attain a strain-tolerant columnar grain structure, although other deposition techniques could be used.

The protective layer 24 may be an overlay coating comprising a nickel aluminide intermetallic. The nickel aluminide intermetallic may be predominately of beta phase, beta- plus gamma-prime phases, gamma-prime phase, and gamma plus gamma-prime phases, each of which may include further alloying additions such as chromium, zirconium, hafnium, silicon, tantalum, platinum, yttrium, lanthanum, calcium, cobalt, rhenium, singly or in combination.The protective layer 24 includes a continuous adherent thermally grown oxide (TGO) or alumina scale 28 formed in situ on the protective layer 24 that adheres the ceramic layer 26. The TGO increases the adherence of the ceramic layer 26, and reduces diffusion of oxygen through the TGO, thereby reducing the oxidation rate. During formation of the TGO, the alumina may comprise meta-stable alumina (i.e., theta- or gamma-alumina) or stable alumina (i.e., alpha-alumina). The alumina phase that is initially formed is dependent on temperature, time, exposure environment, specimen composition and surface finish. The methods disclosed herein provide for controlled growth of the alpha-alumina scale 28 on the surface of the protective layer 24 to resist spallation, cracking or other TBC failure, particularly at the bond coat/ceramic layer interface.

It has been found that increased oxidation resistance and reduced spallation of the ceramic layer 26 is promoted by forming the alumina scale 28 on the disclosed overlay coatings (i.e., protective layer 24) in a manner that is conducive to formation of stable α-alumina rather than the meta-stable alumina (i.e., gamma-, and theta-alumina).

In an exemplary embodiment, a surface of the substrate 22 is coated with a protective layer 24. In an exemplary embodiment, the protective layer 24 may be an overlay coating predominantly of beta-phase intermetallic NiAl.

For example, U.S. Patent No. 6,682,827 discloses a beta-phase NiAl intermetallic overlay coating containing nickel and, in atomic percent, about 30% to about 60% aluminum and about 1% to about 12% platinum-group metal. The overlay coating consists essentially of intermetallic phases of beta-phase NiAl and platinum-group intermetallic phases. Other disclosed overlay coatings include an overlay coating consisting essentially of, in atomic percent, 30% to 60% aluminum, about 5% to about 12% platinum, about 2% to about 15% chromium, about 0.1% to about 1.2%

zirconium, the balance essentially nickel. U.S. Patent No. 6,579,627 discloses a predominantly beta phase intermetallic NiAl overlay coating comprising nickel, from about 20 to about 35 weight percent aluminum, and at least two modifying elements (i.e., zirconium, hafnium, yttrium, and silicon). U.S. Patent No. 6,153,313 discloses a predominantly beta phase NiAl intermetallic overlay coating consisting of 30 to 60 atomic percent aluminum, at least one of chromium, titanium, hafnium, and optionally tantalum, silicon, gallium, zirconium, calcium, iron, and yttrium, the balance nickel and impurities. U.S. Patent No. 6,291,084 discloses a beta-phase NiAl intermetallic overlay coating including 30% to 60% aluminum, 2% to 15% chromium, 0.1% to 1.2% zirconium, and the balance essentially nickel. U.S. Patent No. 6,255,001 discloses a bond coat comprising a NiAl alloy of predominately the beta phase, containing at least 0.2 atomic percent zirconium, and has an average grain size of less than 3 micrometers.

In other exemplary embodiments, the protective layer 24 may be an overlay coating predominantly of gamma prime-phase intermetallic nickel aluminide (Ni_3Al). For example, in U.S. Publication No. 2006/0093752 the overlay coating may contain nickel aluminide intermetallic predominantly of the gamma prime phase and at least one platinum group metal. The exemplary overlay coating may further contain chromium. The exemplary overlay coating may contain at least one reactive element. Other exemplary overlay coatings predominantly of gamma prime-phase intermetallic nickel aluminide (Ni_3Al) are disclosed in U.S. Publication No. 2006/0093850. For example, the overlay coating may contain an as-deposited composition comprising, by weight, at least 6% to about 15% aluminum, about 2% to about 5% chromium, optionally up to 4% of at least one reactive element, optionally up to 2% silicon, optionally up to 60% of at least one platinum group metal, and the balance essentially nickel and incidental impurities.

In other exemplary embodiments, the protective layer 24 may be an overlay coating predominantly of beta- plus gamma prime-phase intermetallic nickel aluminide. For example, in U.S. Publication No. 2006/0093801 an exemplary overlay coating comprises, by weight, at least 14% aluminum. An exemplary overlay coating further comprises up to about 4 weight percent of a reactive element such as zirconium,

hafnium, yttrium, and cerium. In an exemplary overlay coating, about 10 to about 85 volume percent of the coating consists of the gamma-prime nickel aluminide intermetallic phase, and the balance of the coating consists of the beta nickel aluminide intermetallic phase.

In other exemplary embodiments, the protective layer 24 may be an overlay coating predominantly of gamma- plus gamma prime-phase intermetallic nickel aluminide. For example, U.S. Publication No. 2004/0229075 discloses overlay coatings containing, in atomic %, less than 23% aluminum, 10 to 60% platinum, and 0.3 to 2% of a reactive element.

The coated substrate is subjected to controlled environmental conditions conducive to formation of the alpha- phase for the alumina scale 28. In one exemplary embodiment, the coated substrate 22 is pre-oxidized, in a coating deposition chamber, at an elevated temperature (as compared to prior TBC deposition processes), and for a longer duration (as compared to prior TBC deposition processes). For example, the coated substrate may be pre-oxidized in the chamber at temperatures around 2000 °F for about 2 to about 8 hours to achieve a controlled TGO comprising predominantly alpha-alumina scale. The applied temperature may range from greater than about 1900 °F (1038 °C)to about 2200 °F (1204 °C). In other embodiments, the applied temperature may range from about 2000 °F (1093 °C) to about 2150 °F (1178 °C). In prior TBC deposition processes, bond-coated articles are pre-heated to about 1700 °F (927 °C) to about 2000 °F (1093 °C) for about 10 minutes to about 30 minutes in preparation for reception of the ceramic layer. However, these prior conditions are not conducive to initial alpha-alumina formation on the surface of the protective layer 24. Thus, it is beneficial to initially form the stable alpha-alumina on the surface of the protective layer prior to subsequent pre-heating process steps. The initial formation of alpha-alumina avoids the volumetric changes that would occur during the pre-heating process if the alumina scale were predominantly a meta-stable form. Additionally, alpha-alumina has the lowest diffusivity of oxygen among the various forms of aluminas, and consequently the slowest growth rate of the oxide scale.

In another exemplary embodiment, the coated substrate 22 is pre-oxidized in a vacuum furnace at the temperature and time sufficient to provide the desired alpha alumina scale. In an exemplary embodiment, the pre-oxidizing treatment includes about two to about eight hours or an intervening interval, at temperatures from about at least 1900 °F (1038 °C) to about 2150 °F (1178 °C). In an exemplary embodiment, the vacuum furnace is operated at from about 10^{-3} to about 10^{-6} Torr. Alternately, the pre-oxidizing treatment may occur in an atmosphere of air, oxygen, argon, or hydrogen gas containing oxygen. The applied temperature may range from greater than about 1900 °F (1038 °C) to about 2200 °F (1204 °C). In other embodiments, the applied temperature may range from about 2000 °F (1093 °C) to at least about 2150 °F (1178 °C). The temperature, pressure, time and atmospheric conditions are chosen for the particular bond coat/substrate combination in order to maximize alpha alumina formation.

In an exemplary embodiment, the coated substrate undergoes a surface preparation prior to the pre-oxidation of the applied protective layer. The surface treatment modifies at least a portion of the overlay coating for later reception of the thermally insulating ceramic layer 26. The surface treatment may include, for example, chemical milling, chemical milling plus vapor honing, grit blasting, and the like.

In an exemplary embodiment, subsequent to a pre-oxidation treatment, a ceramic layer 26 may be applied to the coated substrate. If the pre-oxidation treatment occurred in a vacuum furnace or other chamber, the coated substrate is then moved to the coating deposition chamber for application of the ceramic layer 26.

In an exemplary embodiment, the pre-oxidized, coated substrate is pre-heated at temperatures from about 1800 °F (982 °C) to about 1900 °F (1038 °C) for about 10 to about 30 minutes before receiving the thermally insulating ceramic barrier coat. Since the coated substrate has been pre-oxidized to provide a predominantly stable alpha-alumina scale, volumetric and other metallurgical transformations are minimized during the pre-heat cycle.

EXAMPLE:

Furnace cycle test specimens of 1 inch diameter x 0.125 inch thick (24.5 mm x 3.175 mm) comprising Rene N5 superalloy substrate were coated with a predominantly beta phase-containing overlay coating by an ion plasma deposition method. The nominal composition of the coating after deposition, in wt %, was 20 –24 % Al, 5-6 % Cr, about 0.5 – 1 % Zr, with the balance being Ni.

The test specimens were subjected to various heat treat and pre-oxidation conditions as shown in Table 1. A 7wt% Y_2O_3 containing zirconia (YSZ) thermal barrier coating was applied by EB-PVD to a thickness of about 5 mil (127 microns).

In a furnace cycle test, the specimens were heated to 2125 °F (1163 °C), held for about 45 minutes, and then cooled to ambient temperature. This one-hour cycle was repeated to determine TBC spallation life, with 20% spallation as the failure criteria. The results are reflected in FIG. 3. As illustrated, the samples subjected to a pre-oxidation treatment exhibited improved spallation resistance.

TABLE 1

Category	Diffusion Heat Treatment	Pre-Oxidation Surface Treatment	Pre-Oxidation Heat Treatment	Post Oxidation Surface Treatment	Post TBC Heat Treatment
Base	1975 °F for 4 hours at $8x10^{-4}$ Torr	---	---	Ensolve clean and 220 grit at 25 psi	---
Base with Pre-Ox	1975 °F for 4 hours at $8x10^{-4}$ Torr	220 grit at 40 psi	2050 °F for 4 hours at $3x10^{-6}$ Torr	Ensolve clean	---
Base w/Post Ox	1975 °F for 4 hours at $8x10^{-4}$ Torr	---	---	Ensolve clean and 220 grit at 25 psi	2050 °F for 4 hours in air
Vacuum Pre-Ox	---	220 grit at 40 psi	2050 °F for 4 hours at $3x10^{-6}$ Torr	Ensolve clean	---
Air Pre-Ox	---	220 grit at 40 psi	2050 °F for 4 hours in air	Ensolve clean	---

This written description uses examples to disclose the invention including the best mode, and to enable any person skilled in the art to make and use the invention. The patentable scope of the invention is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from

the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

WHAT IS CLAIMED IS:

CLAIMS

1. A method characterized by:

a) providing a coated superalloy substrate with an overlay coating on at least one surface, wherein the overlay coating is selected from the group consisting of a nickel aluminide intermetallic predominantly of beta phase, a nickel aluminide intermetallic predominantly of beta plus gamma prime phases, a nickel aluminide intermetallic predominantly of gamma plus gamma prime phases, and a nickel aluminide intermetallic predominantly of gamma prime phase; and

b) subsequent to (a), subjecting the coated substrate to predetermined conditions to grow an aluminum oxide scale on the selected overlay coating, wherein the aluminum oxide comprises predominantly alpha phase alumina.

2. The method according to claim 1 wherein in (b), subjecting the coated substrate to the predetermined conditions includes:

heating the coated substrate to at least 1038 °C to 1204 °C for a time sufficient to provide the predominantly alpha phase alumina.

3. The method according to any of the claims 1 and 2 wherein during at least a part of (b), the coated substrate is heated under a vacuum of between 10^{-3} and 10^{-6} Torr.

4. The method according to any of the claims 1 and 2 wherein during at least a part of (b), the coated substrate is heated in an atmosphere of air, oxygen, argon, or hydrogen gas.

5. The method according to any of the claims 1, 2, 3 and 4 and further comprising:

(c) subsequent to (b), providing a thermally insulating ceramic layer on the overlay coating.

6. The method according to any of the claims 1, 2, 3, 4 and 5 wherein in (a), providing the substrate with the overlay coating includes depositing the selected overlay coating on the at least one surface by a physical vapor deposition technique.

7. The method according to any of the claims 1, 2, 3,4, and 5 wherein in (a), the nickel aluminide intermetallic comprises at least one of chromium, zirconium, hafnium, silicon, tantalum, platinum, yttrium, lanthanum, calcium, cobalt, and rhenium.

8. The method according to any of the claims 1, 2, 3, and 4 and further comprising:

(c) subsequent to (b), positioning the coated substrate in a coating deposition chamber;

(d) heating the coated substrate from 925 °C to 1093 °C in the coating deposition chamber for at least 10 minutes to 30 minutes; and

(e) subsequent to (d), providing a thermally insulating ceramic layer on the overlay coating.

9. The method according to any of the claims 1, 2, 3, and 4 and further comprising:

(c) prior to (b), physically modifying at least a portion of the overlay coating by at least one technique selected from milling, honing, and grit blasting.

10. A method characterized by:

a) providing a coated superalloy substrate with an overlay coating on at least one surface, wherein the overlay coating is a nickel aluminide intermetallic predominantly of beta phase, a nickel aluminide intermetallic predominantly of beta plus gamma prime phases, a nickel aluminide intermetallic predominantly of gamma plus gamma prime phases, a nickel aluminide intermetallic predominantly of beta plus gamma phases, or a nickel aluminide intermetallic predominantly of gamma prime phase;

b) subsequent to (a), physically modifying at least a portion of the selected overlay coating by milling, honing, or grit blasting;

c) subsequent to (b), heating the coated substrate in a vacuum chamber at a temperature of at least 1093 °C to 1150 °C, for from 2 to 4 hours, under a vacuum of from 10^{-3} to 10^{-6} Torr to grow an aluminum oxide scale on the selected overlay coating, wherein the aluminum oxide comprises predominantly alpha phase alumina;

d) subsequent to (c), pre-heating the coated substrate in a deposition chamber at a temperature of from 925 °C to 1093 °C for from 10 to 30 minutes; and

e) subsequent to (d), depositing a thermally insulating ceramic layer on the overlay coating.