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(54) Title: MULTILAYER THERMAL BARRIER COATINGS

(57) **Abrégé/Abstract:**

The present invention relates to a thin impermeable top coat on a thermal barrier coating for a metal part, such as a turbine blade, wherein the composite thin top coat is a porous, inert, non-sacrificial, less permeable ceramic layer that eliminates the infiltration of environmental contaminants into the thermal barrier coating during operation of the metal part, thereby extending the life of the underlying thermal barrier coating and metal part thereunder.



ABSTRACT

The present invention relates to a thin impermeable top coat on a thermal barrier coating for a metal part, such as a turbine blade, wherein the composite thin top coat is a porous, inert, non-sacrificial, less permeable ceramic layer that eliminates the infiltration of environmental contaminants into the thermal barrier coating during operation of the metal part, thereby extending the life of the underlying thermal barrier coating and metal part thereunder.

MULTILAYER THERMAL BARRIER COATINGS

FIELD OF THE INVENTION

The present invention relates to multilayer thermal barrier coatings for high performance metal parts, with an increased resistance to environmental contaminants at high temperature conditions. In particular, the present invention relates to a thin impermeable top coat on a thermal barrier coating for a metal part, such as a turbine blade, wherein the composite thin top coat is a porous, inert, non-sacrificial, less permeable ceramic layer that eliminates the infiltration of environmental contaminants into the thermal barrier coating during operation of the metal part, thereby extending the life of the underlying thermal barrier coating and metal part thereunder.

BACKGROUND OF THE INVENTION

Thermal barrier coatings are deposited onto gas turbine vanes, blades, combustion liners and other heat engine parts to reduce the heat flow into the coated metal part during operation of the engine, and to allow the metal part to run cooler than the gas stream, thereby extending part life and resulting in a higher combustion efficiency by permitting higher gas temperatures.

Conventionally, thermal barrier coatings are deposited onto metal alloy parts, whereby the thermal barrier coating prolongs the life of the underlying metal part. Since gas turbine engines and other high temperature and high pressure engines operate under harsh stressed environments, thermal barrier coatings are often deposited onto the outer surface of metal alloy parts to impede the damage caused by such an extreme operating environment.

At high temperature operating conditions, environmental contaminants deposit onto the surface of thermal barrier coated metal alloy parts of gas turbine engines. At high temperatures, these deposited contaminants may become molten liquids that infiltrate the thermal barrier coating. Subsequent to the infiltration of contaminants and upon cooling, these molten contaminants solidify and build stress within the thermal barrier coating. The stress that builds up generates cracks which lead to the subsequent failure of the protective thermal barrier coating. Moreover, molten contaminants can chemically react with thermal barrier coatings, thereby chemically dissolving the protective thermal barrier coating. Such thermal barrier coatings are said to be sacrificial, because with repeated exposure to molten contaminant environments, the thermal barrier coating chemically reacts with the contaminant environment and is depleted over time.

Therefore, chemical and mechanical interactions may occur between contaminant environments and thermal barrier coatings, such that, under high temperature operating conditions, molten environmental contaminants can deposit and subsequently dissolve or permeate the thermal barrier coating, thereby resulting in the progressive loss of the protective thermal barrier coating.

It is therefore desirable to prevent the damage and subsequent depletion of thermal barrier coatings by the reaction with, or infiltration of, molten contaminants during the operation of high temperature engines.

DESCRIPTION OF THE RELATED ART

The prior art describes various thermal barrier coatings which aim to impede or reduce damage to the metal parts of high temperature engines. Conventionally, thermal barrier coatings are comprised of ceramic material, such as chemically-stabilized zirconia, including yttria-stabilized zirconia (YSZ), scandia-stabilized zirconia, calcia-stabilized zirconia and magnesium-stabilized zirconia, with YSZ being the thermal barrier coating of choice. United States Patent No. 5,871,820 issued to Hasz et al on February 16, 1999 describes a method for protecting thermal barrier coatings from environmental contaminants on metal engine parts at operating temperatures through the deposition of an impermeable, non-porous barrier coating onto the surface of a thermal barrier coating. United States Patent No. 5,851,678, also issued to Hasz et al on December 22, 1998, describes a composite thermal barrier coating with a non-porous, impermeable barrier coating. Both Hasz et al patents disclose thermal barrier coatings comprised of the same group of chemically-stabilized zirconia.

Similar to the above mentioned Hasz et al patents, United States Patent No. 5,773,141 issued to Hasz et al on June 30, 1998 describes the provision of a single protective layer of a sacrificial or reactive oxide that overlays the outer surface of the thermal barrier coating, thereby impeding damage to the thermal barrier coating during use. The composition of the single protective sacrificial layer surrounding the thermal barrier coating is dependent partly on the composition of the environmental contaminants and on the surface temperature of the thermal barrier coating during operation. The sacrificial protective layer deposited onto the thermal barrier coating in United States Patent No. 5,773,141 is said to be sacrificial because it reacts with the contaminant environment and attempts to reduce the temperature at the environment barrier interface. Since this protective layer reacts with the environment and is progressively depleted with continuous use, it is said to be sacrificial, and will protect the thermal barrier coating for an limited period of time.

Since thermal barrier coatings protect the metal parts of high temperature operation engines, it is desirable that thermal barrier coatings be long-wearing. Moreover, it is preferable that the thermal barrier coating be shielded with a non-sacrificial, non-reactive protective layer that does not deplete over time and prevents or reduces the infiltration of environmental contaminants into the thermal barrier coating.

There are many patents in the prior art that propose thermal barrier coatings of various compositions, and some patents even propose to protect the thermal barrier coating with a temporary coating. However, there is no teaching in the prior art that describes a multilayer thermal barrier coating that is coated with a thin, inert, non-sacrificial oxide top layer that does not deplete or react with the surrounding environment, and is capable of protectively shielding the thermal barrier coating it encases indefinitely from high temperature operation and thermal cycling.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an article with increased resistance to environmental contaminants under high temperature conditions, wherein the article is comprised of a metal alloy part, a protective thermal barrier coating, and a thin porous, inert, non-sacrificial protective top coat deposited thereon.

In accordance with the present invention, the metal alloy part, which may also be referred to as the parent material, may be of any material used in the construction of engine parts. The metal alloy part may be comprised cobalt, iron, chromium, nickel, aluminum, or any other appropriate metal alloy material. In addition, the metal bond coat, which may also be referred to as the inner metal alloy bond coat of the thermal barrier coating, may be comprised of a metal superalloy, or a metal alloy comprised of cobalt, iron, chromium, nickel, aluminum, or any other appropriate metal alloy material. Alternatively, the metal bond coat may be omitted from the thermal barrier coating, such that the metal alloy part is coated with a ceramic thermal barrier coat onto which the inventive protective top layer according to the present invention is deposited thereon.

Therefore, in accordance with the present invention, a metal alloy part is protected against attack from environmental contaminants under high temperature and high pressure environments, such that the metal alloy part is encased or covered with a thermal barrier coating that is deposited thereon. In accordance with the present invention, a non-sacrificial, inert, protective, thin ceramic top coat is deposited onto the thermal barrier coating that overlays a metal alloy part.

In accordance with the present invention, the protective, inert, non-sacrificial thin ceramic top coat comprises ceria-stabilized zirconia (CSZ), calcium silicate zirconate (CaSZ), zirconia toughened alumina (ZTA), compound oxides, mullite materials or a mixture of two or more thereof. Moreover, in accordance with the present invention the said compound oxides of the protective top coat may comprise two or more compounds from the group consisting of aluminum, cobalt, chromium, iron, titanium or nickel, whereby in addition to oxygen, aluminum, cobalt, chromium, iron, titanium and/or nickel are major elemental constituents.

The thermal barrier coating that underlies the thin ceramic top coat of the present invention may be comprised of a base ceramic coating and an inner metal alloy bond coat, such that the inner metal alloy bond coat of the thermal barrier coating is deposited onto the metal alloy part and the base ceramic coating of the thermal barrier coating is deposited onto the inner metal alloy bond coat. Moreover, in another embodiment of the present invention, the thermal barrier coating may be comprised of a base ceramic coating, wherein the base ceramic coating is deposited directly onto the metal alloy part, and the thin ceramic top coat of the present invention is deposited thereon.

Therefore, in accordance with the present invention the multilayer coating deposited onto the metal alloy part may comprise, the metal alloy part overlaid with an inner metal alloy bond coat which is overlaid with a base ceramic coat, wherein the inner metal alloy bond coat and the base ceramic coat embody a thermal barrier coating, which is overlaid with the thin ceramic top coat of the present invention. Moreover, for example, in another embodiment of the present invention the multilayer coating deposited onto the metal alloy part may comprise, the metal alloy part overlaid with a base ceramic coat, wherein the base ceramic coat embodies a thermal barrier coating, which is overlaid with the thin ceramic top coat of the present invention.

The base ceramic coating of the protective thermal coating may comprise yttria-stabilized zirconia (YSZ), alumina-titania, calcia stabilized-zirconia, magnesia stabilized-zirconia, ceria-stabilized zirconia (CSZ), scandia stabilized-zirconia, calcium silicate, calcium silicate zirconate blends, calcium-stabilized zirconia (CaSZ), zirconia toughened alumina (ZTA), alumina-zirconia, zirconium silicate, zircon, alumina or blends thereof.

The ceramic coat of the thermal barrier coating and the inventive ceramic protective top layer are mutually dissimilar ceramic coats in any individual multilayer coating. For example, the ceramic coating of the thermal barrier coat deposited onto a metal alloy part may be yttria-stabilized zirconia (YSZ) while the inventive protective top layer deposited

thereon may be ceria-stabilized zirconia (CSZ). That is to say, for example, when the ceramic coat of the thermal barrier coat is yttria-stabilized zirconia (YSZ) the inventive protective top layer deposited thereon must be a material other than yttria-stabilized zirconia (YSZ).

Accordingly, the present invention provides an article having an increased resistance to attack from environmental contaminants, wherein said environmental contaminants comprise oxygen, sodium, chlorine and saline mixtures, water vapour, vanadium, sulfur and similar contaminants under high temperature conditions, comprising: a metal alloy part; a protective thermal barrier coating thereon comprising an optional inner metal alloy bond coating surmounted by an outer ceramic coating; and a porous, non-sacrificial, ceramic top layer comprising: ceria-stabilized zirconia (CSZ); calcium-stabilized zirconia (CaSZ); zirconia toughened alumina (ZTA); compound oxides containing two or more compounds from the group consisting of aluminum, cobalt, chromium, iron, titanium or nickel, in which, in addition to oxygen, aluminum, cobalt, chromium, iron, titanium and/or nickel are major elemental constituents; mullite materials; or a mixture of two or more thereof.

The environmental contaminants from which the article may be protected include high temperature, high pressure environments consisting of or containing oxygen, sodium, chlorine and saline mixtures, water vapour, vanadium, sulfur and similar contaminants. Therefore, the protected metal alloy part according to the present invention, has an increased resistance in high velocity combustion gas streams under continuous long term exposure or thermally cycled conditions at temperatures above 850°C (1560 °F) and even protects at temperatures in excess of 1200°C (2204 °F).

The thermal barrier coating in the articles according to the present invention is comprised of a base ceramic coating of a multilayer coating comprised of an optional inner metal alloy bond coat surmounted by an outer base ceramic coating. The metal alloy bond coat may be any appropriate material, however this metal alloy bond coat is not necessarily essential and may be omitted. The base ceramic coating of the thermal barrier coating, which may also be referred to as the base ceramic coat or base ceramic layer, may be comprised of partially stabilized zirconia stabilized with yttria, calcia, magnesia, ceria or scandia. In addition the outer ceramic layer of the thermal barrier coating may also consist of various grades of alumina and alumina-zirconia. Therefore, the base ceramic coating of the thermal barrier coating may be comprised of yttria-stabilized zirconia (YSZ), alumina-titania, calcia stabilized-zirconia, magnesia stabilized-zirconia, ceria-stabilized zirconia (CSZ), scandia stabilized-zirconia, calcium silicate, calcium silicate zirconate blends, calcium-stabilized zirconia (CaSZ), zirconia toughened alumina (ZTA), alumina-zirconia, zirconium silicate, zircon, alumina or blends thereof.

The thermal barrier coating is subsequently coated in accordance with the present invention, with the thin inventive protective top coat that shields and maintains the integrity of the underlying thermal barrier coating. Both the base ceramic layer and the top protective layer are deposited by thermal spraying (plasma or flame) or from a slurry or by sol-gel techniques. When deposited from a slurry or sol-gel, a subsequent heat treatment will be required to dry the coating and provide the necessary cohesive and adhesive strength.

The inventive thin protective top coat that covers and preserves the thermal barrier coating is a porous, protective, inert, non-sacrificial ceramic top layer comprised of ceria-stabilized zirconia (CSZ), calcium silicate zirconate (CaSZ), zirconia toughened alumina (ZTA), compound oxides, mullite materials or blends thereof. In accordance with the present invention the said compound oxides of the protective top coat consists of two or more compounds from the group consisting of aluminum, cobalt, chromium, iron, titanium or nickel, whereby in addition to oxygen, aluminum, cobalt, chromium, iron, titanium and nickel are major elemental constituents. This layer is preferably deposited by plasma or flame thermal spray processes, however, slurry and sol-gel techniques may be used as well, with a subsequent heat treatment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The degradation or depletion of protective thermal barrier coatings by molten environmental contaminants is significantly prevented by the deposition of the thin protective shielding top coat of the present invention. The inventive protective top coat covers and encases the lower thermal barrier coating, thereby substantially reducing the rate of infiltration of molten environmental contaminants into the thermal barrier coating. Furthermore, the inventive protective top coat minimises the chemical interaction of the contaminant environment with the thermal barrier coating, thereby significantly slowing down the chemical dissolution of the thermal barrier coating at high operating temperatures.

Since the protective top coat of the present invention prevents the penetration of molten environmental contaminants into the thermal barrier coating, the integrity of the thermal barrier coating is not affected. Therefore, since the life of the thermal barrier coating is prolonged significantly, the probability of part failure is substantially reduced.

The inventive protective top coat prolongs the life of the thermal barrier coating because the protective top coat has a higher resistance to erosion, fracture or corrosion with respect to the lower ceramic thermal barrier coat. The protective top coat according to the

present invention is a thin layer that encases and shields the thermal barrier coating thereunder. The base ceramic coat, which is deposited by thermal spraying, slurry or sol-gel techniques, is a porous coating. The base ceramic coat usually contains a degree of porosity ranging from 3-20%, such that these pores and the small micro-cracks also present are not well-connected. Therefore, environmental contaminants do not have a ready path from the coating surface to the metal-ceramic interface. In the absence of a top coat, according to the present invention, these small micro-cracks would quickly lengthen and subsequently provide an easy, or more direct path for corrodents to reach the metal surface. The propagation, and extension of micro-cracks is due to a combination of operating factors including, but not limited to, high temperature, high pressure, coating erosion by particulates, particle impact, and chemical reactions leading to thermal expansion mismatch stress. Some gaseous species may also react with the base ceramic layer to form molten salts that may effectively penetrate these micro-cracks and connected pores. Subsequent failure of the coating, which is also referred to as delamination or spalling, is a result of the corrosion of the metal at the metal-ceramic interface or within the ceramic layer adjacent to the metal. The thin protective top coat according to the present invention, significantly reduces the rate of, or prevents the infiltration of contaminants via the micro-cracks to the ceramic-metal interface

In addition, the protective top coat of the present invention is characteristically not dense. The protective top coat of the present invention is a porous, continuous, relatively impermeable layer. Moreover, the protective top coat of the present invention has a degree of porosity ranging from 1-20 % by volume, where the preferred degree of porosity is preferably 3-10 % by volume.

The reduction or prevention of contaminants into the thermal barrier coating reduces the occurrence of fracture at or near the thermal barrier coat-metal interface, which may also be referred to as the ceramic-metal interface. The reduction and prevention of the infiltration of contaminants into the ceramic layer of the thermal barrier coating and the subsequent infiltration of contaminants at or near the interface of the ceramic layer of the thermal barrier coat and the metal of the underlying metal alloy part reduces the occurrence of delamination, prevents failure of the thermal barrier coating and consequently maintains the integrity of the thermal barrier coating and extends the life of the metal alloy part.

In accordance with the present invention, the protective top coat may be comprised of ceria-stabilized zirconia (CSZ); calcium silicate zirconate (CaSZ); zirconia toughened alumina (ZTA); compound oxides which include, in addition to oxygen, two or more compounds from the group consisting of aluminum, cobalt, chromium, iron, titanium or nickel as major elemental constituents; mullite materials or blends thereof. It should be noted

that the properties of the protective top coats are not all identical. The selection of which protective top coat will be deposited onto the thermal barrier coat should be based on the specific needs and use requirements of the thermal barrier coated metal alloy part. For example, at temperatures less than 1000°C (1832°F) a protective top coat of calcium silicate zirconate (CaSZ) or compound oxides may provide better protection than a protective top coat of ceria-stabilized zirconia (CSZ) or zirconia toughened alumina (ZTA), whereas the reverse may be true at temperatures exceeding 1000°C (1832°F).

In accordance with the present invention, the protective top coat does not react with, and does not need to react with, environmental contaminants to protect the underlying thermal barrier coating. The inertness of the present protective top coat to the contaminant environment enables the protective top coat of the present invention the ability to protect the underlying thermal barrier coating indefinitely since it does not chemically or physically deplete with repeated use. Contrary to protective top coats of the prior art, which temporarily protect the underlying thermal barrier coating by reacting with the environmental contaminants in an attempt to reduce the temperature at the environment-barrier interface or to prevent the migration of contaminants into the base ceramic coating and into the metal surface, the protective top coat of the present invention does not react with the contaminant environment. Since the protective top coat of the present invention is inert to the contaminant environment, it is not depleted and is able to indefinitely shield the thermal barrier coating thereunder. Ultimately, failure of the base ceramic coat occurs at or near the base ceramic-metal interface, however, this failure of the base coating occurs before the degradation of the thin protective top coat of the present invention.

Moreover, the integrity of the protective top coat of the present invention is maintained even upon failure of the thermal barrier coat. Patents of the prior art, however, disclose that only after the consumption or depletion of the sacrificial top coat does the failure of the thermal barrier coat occur. Therefore, contrary to the prior art, the protective top coat of the present invention is not consumed prior to failure. The thin protective top coat of the present invention protects the base ceramic in several ways, depending on the environmental contaminant species and conditions present. Since the thin protective top coat of the present invention does not react with environmental corrodents, deposition of these species on the surface is discouraged, and therefore, the subsequent migration of these species into the base ceramic layer is accordingly minimised. In addition, since most of the contaminants that may deposit onto the surface of the thin protective top coat of the present invention are only loosely adhered to the surface, most of these contaminants are quickly removed or blown off by the flowing high velocity gas propelled thereover, or during the cool down and the consequent differential thermal expansion. In environments where particulate impact or

erosion may occur, a higher resistance in the thin protective top layer of the present invention reduces the rate of microcracking of the base ceramic layer, thereby extending the life of the coating.

Environmental contaminants may include oxygen, sodium, chlorine, and saline mixtures, water vapour, sodium, vanadium, sulfur and similar contaminants. Under normal room temperature conditions, these and other environmental contaminants are not damaging to the thermal barrier coatings. However, under high temperature, high pressure conditions, these and other environmental contaminants, once deposited onto the thermal barrier coating can become molten liquids that can permeate into the thermal barrier coating. Therefore, to prevent this infiltration of molten contaminants, the inventive protective layer of the present invention is deposited onto the surface of thermal barrier coatings, thereby precluding the infiltration of these and other molten contaminants into the thermal barrier coat. As a result, the life of the thermal barrier coating and the coated metal part is prolonged indefinitely.

It should be noted that the environmental contaminants of combustion atmospheres or hot air atmospheres containing oxygen, sodium, chlorine, saline mixtures, water vapour, sodium, vanadium, sulfur and similar contaminants are such that the contaminant levels are low. For example, excluding oxygen, the total contaminant level may be less than approximately 20 % by volume.

The protective top coat of the present invention acts as a protective shield to the thermal barrier coating, thereby protecting the thermal barrier coating it encases against surrounding contaminant environments. More specifically, the present protective top coat preferably preserves the coated thermal barrier coating from the contaminant environments of operating gas turbines. However, the present protective coating is not limited to the operating environment of gas turbines. The protective coat of the present invention may also be suitable for hot section gas turbine parts as well as other machine parts, which may encounter high operating temperatures or undergo thermal cycling. For example, the present protective coating may serve as a useful protective coating in a variety of industrial fields, such as steam engines, boilers, standard air engines, marine atmospheres, petrochemical and metal refineries.

The protective coating of the present invention may be described as a porous, non-dense, non-sacrificial, inert, thin and relatively impermeable ceramic layer that prevents molten liquid contaminants from contacting the thermal barrier coating it encases. The protective top coat of the present invention does not undergo any chemical or physical interaction with the surrounding contaminant environment, whereby the said top coat

precludes the chemical or physical interaction of molten contaminants with the thermal barrier coating. Therefore, the thin protective top coat of the present invention acts as a relatively impermeable barrier between environmental contaminants and the thermal barrier coating.

Furthermore, the protective top coat according to the present invention is a continuous thin ceramic coating. The thickness of the protective top coat may vary, but the preferred thickness is essentially determined by the amount of protective coating needed to prevent the infiltration of environmental contaminants into the thermal barrier coat. The protective top coat of the present invention is thin with respect to the ceramic layer of the thermal barrier coating it encases. The protective top coat is approximately 5x thinner when compared to the ceramic layer of the thermal barrier coating thereunder. Preferably the thickness of the inventive protective coating may be approximately 25-125 microns (0.001-0.005") whereas the ceramic layer of the thermal barrier coating may be approximately 75-500 microns (0.003-0.020").

Furthermore, experimental results indicate that a thicker protective top coat does not necessarily extend the life of the thermal barrier coating. For example, an increased total ceramic thickness, that is the thickness of the ceramic protective top coat and the thickness of the ceramic layer of the thermal barrier coating may contribute to an increased sensitivity to thermal spalling, or a restriction in the proper flow of the combustion gases. In general the thicker the top coat, the more susceptible it is to failure due to fracture at the ceramic-metal interface or delamination under thermal cycling.

Moreover, the use of a ceramic coat, such as YSZ, is additionally used to reduce the temperature of the underlying metal part. That is to say, the ceramic coat of the thermal barrier coat, or the thermal barrier coat impart a heat buffering element, or a thermal insulation to the underlying metal part. In accordance with the present invention, the base coat of the thermal barrier coating may be comprised of yttria-stabilized zirconia (YSZ), alumina-titania, calcia stabilized-zirconia, magnesia stabilized-zirconia, ceria-stabilized zirconia (CSZ), scandia stabilized-zirconia, calcium silicate, calcium silicate zirconate blends, calcium-stabilized zirconia (CaSZ), zirconia toughened alumina (ZTA), alumina-zirconia, zirconium silicate, zircon, alumina or blends thereof, wherein YSZ is a preferred ceramic coat. In addition to its superior thermal insulating ability, YSZ also exhibits excellent adhesion properties under thermal cycling conditions.

In addition, the thickness of the ceramic protective top coat may also be affected, whereby, certain operating conditions, such as various temperature combinations, and various

temperature and corrodent combinations, may necessitate the application of a thicker protective top coat. These conditions are more likely to occur in some industrial manufacturing conditions rather than in gas turbine operating environments. It should be noted that, if a thicker protective layer according to the present invention is required, the inventive protective layer and the lower thermal barrier coat may be graded to minimize internal stress.

The protective top coat of the present invention is deposited onto the outer surface of the thermal barrier coating that surmounts a metal alloy part of a gas turbine engine or the like. The protective ceramic top coat, of the present invention does not chemically react with the molten environmental contaminants. Therefore, the protective top coat of the present invention is not depleted, and does not chemically dissolve with repeated high temperature operation. Therefore, since the protective layer of the present invention is not sacrificial, and remains intact with repeated, prolonged use, and since it covers the thermal barrier coating thereunder, it ensures that the integrity of the thermal barrier coating it encases is indefinitely maintained.

The protective layer of the present invention may be applied onto the outer surface of a thermal barrier coating, where the thermal barrier coating may be comprised of yttria-stabilized zirconia (YSZ), alumina-titania, calcia stabilized-zirconia, magnesia stabilized-zirconia, ceria-stabilized zirconia (CSZ), scandia stabilized-zirconia, calcium silicate, calcium silicate zirconate blends, calcium-stabilized zirconia (CaSZ), zirconia toughened alumina (ZTA), alumina-zirconia, zirconium silicate, zircon, alumina or blends thereof. The thermal barrier coating provides thermal insulation to base metal alloys of gas turbine engines, or other metal surfaces for use in high temperature, high velocity, or high pressure gas environments.

The thermal barrier coating may be comprised of a single layer or of two or more layers, whereby a lower metal coat provides corrosion resistance and an adjacent upper or base ceramic layer is a main thermal protector. In accordance with the present invention, thermal barrier coats are indefinitely protected by way of the additional coating with the thin, less permeable protective top coat of the present invention. As a result, the present invention describes a two or three layer, or multilayer composite coated thermal barrier coating. Thus, the overall thermal barrier coating of the present invention is comprised of one or two or more layers, comprised of an optional inner metal alloy bond coat which is surmounted by an outer base ceramic coating, which is then shielded or covered with a thin protective top coat according to the present invention.

The protective top coat of the present invention is a non-sacrificial, less permeable ceramic layer. This protective top coat or barrier precludes the infiltration of molten contaminants into the thermal barrier coating below. Other conventional thermal barrier coatings attempt to reduce the infiltration of environmental contaminants into the thermal barrier coating, however these prior art compositions are sacrificial and are depleted or dissolved over repeated use.

The protective coat of the present invention may be deposited onto the thermal barrier coating by various coating methods known in the art, such as thermal spraying or atmospheric plasma, slurry spraying or cold spraying and physical or chemical vapour deposition. However, the preferred method of depositing the ceramic layer of the thermal barrier coating and the protective top coat is by thermal spraying with air or atmospheric plasma. It should be noted that ceramic slurries may be applied by means of brushing, dipping, spraying or any other means that allows for a desirable application. Moreover, subsequent to deposition, thermal treatment may be required to provide adequate adhesion of this layer with the base ceramic layer of the thermal barrier coat.

The following Examples illustrate the benefits of the protective layer of the present invention.

EXAMPLE I

A group of superalloy pins were air plasma coated with 500 microns (0.012") thick of yttria-stabilized zirconia (YSZ) while another group of superalloy pins were coated with 500 microns (0.012") thick of zirconia toughened alumina (ZTA), respectively. Some of the YSZ pins were further air plasma coated with a thin layer of ZTA or ceria-stabilized zirconia (CSZ), such that the thin additional coat was less than 50 microns (0.002") thick. The YSZ, ZTA, YSZ-ZTA and YSZ-CSZ superalloy pins were then subjected to thermal cycling in air, using a natural gas burner, to a maximum temperature of 1232°C (2250°F). The pins then underwent a controlled rapid cooling to less than 204°C (400°F) with dry compressed air. Upon examination, both the YSZ and the ZTA coated pins failed after 504 and 433 cycles, respectively, while the pins coated with YSZ-ZTA and with YSZ-CSZ did not fail, even after 600 cycles. This result illustrates the effectiveness of the thin top layer in increasing the spalling or dissolution resistance of the coating material. Moreover, the present Example illustrates that single layer ceramic coats do not last as long as base ceramic coats that have been coated with a thin top layer, irrespective of the base ceramic coat composition, thereby further demonstrating that the thin top coat of the present invention increases the life of the base ceramic coat and therefore, as a result, provides thermal insulation for a prolonged period of time.

EXAMPLE II

A group of superalloy pins were air plasma coated with 75-150 micron (0.003-0.006") thick of yttria-stabilized zirconia (YSZ). Some of the YSZ coated pins were further air plasma coated with a 50-75 micron (0.002-0.003") thick layer of CSZ or calcium silicate zirconate (CaSZ), thereby yielding pins coated with YSZ-CSZ or YSZ-CaSZ, respectively. The YSZ, YSZ-CSZ and YSZ-CaSZ coated pins were then subjected to thermal cycling in air, using a natural gas burner, to a maximum temperature of 1232°C (2250°F). The pins then underwent a controlled rapid cooling to less than 204°C (400°F) with dry compressed air. The pins were then sprayed with a water-based solution of 3% sulfur, 3% sodium and 1% vanadium. Upon examination, the pins without the protective top coat, i.e. the YSZ coated pins failed after 130-150 cycles, while the coated pins, i.e. the YSZ-CSZ and YSZ-CaSZ pins did not fail even after over 200 cycles. It was further noted that, for both the YSZ-CSZ and YSZ-CaSZ coated pins, the top coat did not fail, failure only occurred when the lower YSZ coat fractured away from the base metal coat at the interface between the metal pin and the adjacent YSZ coat. The thin top coat deposited onto the lower YSZ coat did not fail, and remained intact, i.e. the CSZ and CaSZ did not fragment or fracture off the lower YSZ coat. The results of this Example illustrate the protection provided by the thin top coat layer to the thermal cycling process in a salt environment, whereby the protective top coat was non-sacrificial, that is to say, it did not deplete or dissolve during the cycling process. The protective top coat did not fail, and the loss of thermal protection to the underlying superalloy pins only occurred when the lower coat finally failed.

EXAMPLE III

A group of superalloy pins were air plasma coated with ceramic coatings to a total thickness of about 150 microns (0.006"). The three coating types included pins coated with 150 microns (0.006") YSZ only, pins coated with 75-100 microns (0.002-0.004") YSZ plus 50 microns (0.002") CSZ, and pins coated with 75-100 microns (0.003-0.004") YSZ plus 50 microns (0.002") CaSZ, respectively. The YSZ, YSZ-CSZ and YSZ-CaSZ coated pins were then subjected to 53 thermal cycles in air, using a natural gas burner, to a maximum temperature of 1150°C (2100°F). The pins then underwent a controlled rapid cooling to less than 204°C (400°F) with dry compressed air, during which time the pins were sprayed with a water-based solution of 0.5% sulfur, 0.77% chlorine and 0.86% sodium. After these 53 cycles, the thermal cycling conditions were changed to 1177°C (2150°F) max temperature, less than 204°C (400°F) cold temperature, one extra minute of exposure at max temperature, and sprayed with an aqueous solution of 1% vanadium, 3% sulfur and 3% sodium. The single layer YSZ coating failed first; at as low as 53 cycles and at an average of 101 cycles, while the coatings containing a top protective layer did not fail even after 130 cycles. The results of this Example shows that the total ceramic coating thickness is not necessarily a factor in the

protection provided by the top protective layer. All the coatings in this Example had the same total ceramic thickness and, therefore, provided approximately the same thermal insulation protection to the metal.

The above Examples illustrate that the thin top protective coating according to the present invention improves the life of the lower thermal barrier coat. In addition, the protective coat of the present invention is non-sacrificial and does not fail with repeated use. The protective top coat only failed when the lower thermal barrier coat failed.

While preferred embodiments have been described, it will be understood that there is no intent to limit the invention to such disclosure, but rather it is intended to cover all modifications and alternate applications falling within the spirit and scope of the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OF PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An article having increased resistance to attack from environmental contaminants under high temperature conditions, comprising:
 - (i) a metal alloy part,
 - (ii) a protective thermal barrier coating deposited onto said metal alloy part; and
 - (iii) a protective, porous, non-sacrificial, inert, thin ceramic top coat deposited onto said thermal barrier coating, wherein said thin ceramic top coat comprises ceria-stabilized zirconia (CSZ); calcium-stabilized zirconia (CaSZ); zirconia toughened alumina (ZTA); a compound oxide ; a mullite material; or a mixture of two or more thereof.
2. An article according to claim 1, wherein said environmental contaminants comprise oxygen, sodium, chlorine, saline mixtures, water vapour, sodium, vanadium, sulfur and similar contaminants under high temperature and/or high pressure conditions.
3. An article according to claim 1 or 2, wherein said metal alloy part is comprised of cobalt, iron, chromium, nickel, aluminum, or an alloy of two or more thereof.
4. An article according to claim 1, 2 or 3, wherein said protective thermal barrier coating comprises a base ceramic coating and a inner metal alloy bond coat, such that said inner metal alloy bond coat is deposited onto said metal alloy part and said base ceramic coating is deposited onto said inner metal alloy bond coat.
5. An article according to claim 1, 2 or 3, wherein said protective thermal barrier coating comprises a base ceramic coating, and said base ceramic coating is deposited onto said metal alloy part and said thin ceramic top coat is deposited onto said base ceramic coating.
6. An article according to any one of claims 1 to 5, wherein said base ceramic coating of said protective thermal barrier coating comprises yttria-stabilized zirconia (YSZ), alumina-titania, calcia stabilized-zirconia, magnesia stabilized-zirconia, ceria-stabilized zirconia (CSZ), scandia stabilized-zirconia, calcium silicate, calcium silicate zirconate blends, calcium-stabilized zirconia (CaSZ), zirconia toughened alumina (ZTA), alumina-zirconia, zirconium silicate, zircon, alumina or a blend thereof.

7. An article according to any one of claims 1 to 6, wherein said metal alloy part and said metal alloy bond coat of said thermal barrier coating are comprised of a metal superalloy, or a metal alloy comprised of cobalt, iron, chromium, nickel, aluminum, or an alloy of two or more thereof.
8. An article according to any one of claims 1 to 7, wherein said compound oxide comprises two or more compounds from the group consisting of aluminum, cobalt, chromium, iron, titanium or nickel, whereby in addition to oxygen, aluminum, cobalt, chromium, iron, titanium and/or nickel are major elemental constituents.
9. An article according to any one of claims 1 to 8, wherein said base ceramic coat of said thermal barrier coating is dissimilar from said thin ceramic top coat in an individual multilayer coating.
10. An article according to any one of claims 1 to 9, wherein said protective top coat has a thickness of from 25 to 125 (0.001 - 0.005") microns.
11. An article according to any one of claims 1 to 10, wherein said protective top coat has a porosity of from 1 to 20 % by volume.
12. An article according to any one of claims 1 to 10, wherein said protective top coat has a porosity of from 3 to 20 % by volume.
13. An article according to any one of claims 1 to 12, wherein said protective top coat is not substantially dense.
14. An article according to any one of claims 1 to 13, wherein said protective top coat is porous, continuous and relatively impermeable to said environmental contaminants.
15. An article according to any one of claims 1 to 14, wherein said protective top coat is inert to said environmental contaminants, such that said protective top coat does not chemically or physically deplete with repeated use.
16. An article according to any one of claims 1 or 15, wherein the said outer base ceramic coat of the thermal barrier coating has a thickness of from 75 to 500 microns (0.003-0.012").

17. An article according to any one of claims 1 to 16, wherein said high temperature conditions comprise long term exposure and/or thermally cycled conditions above 850°C (1560°F).
18. An article according to claim 17, wherein said high temperature conditions comprise long term exposure and/or thermally cycled conditions above 1200°C (2204°F).
19. An article according to claim 2, wherein said environmental contaminant comprises sodium, chlorine, saline mixtures, water vapour, sodium, vanadium, sulfur and similar contaminants in a concentration approximately less than 20% by volume.
20. An article according to claim 1, wherein the thickness of said protective top coat is approximately five times that of the underlying said thermal barrier coat.
21. An article according to any one of claims 1 to 20, wherein said protective top coat is deposited as a thicker coating, which is graded to minimize internal stresses.
22. An article according to any one of claims 1 to 21, wherein said thermal barrier coating comprises a single layer or a plurality of layers, whereby said thermal barrier coating provides thermal insulation to said underlying metal alloy part.
23. A method of deposition of an article according to any one of claims 1 to 22, wherein said protective top coat or said outer base ceramic coat is applied by thermal plasma spraying or flame spraying, slurry, cold spraying or a sol-gel technique.
24. A method of deposition according to claim 23, wherein the protective top coat or said outer base ceramic coat is thermally sprayed with air or atmospheric plasma.
25. A method of deposition according to claim 23, wherein the protective top coat or said outer base ceramic coat is applied by means of brushing, dipping, or spraying to achieve a substantially uniform coating layer.
26. A method of deposition according to any one of claims 23 to 25, wherein subsequent to the deposition of said protective top coat or said outer base ceramic coat, thermal treatment is effected to enhance the adhesion of the deposited coating layer to the ceramic layer or article thereunder.