

A Method of Treating A Thermal Barrier Coating

Technical Field

The present invention generally relates to method of
5 treating a thermal barrier coating. The present invention
also relates to a system for treating a thermal barrier
coating.

Background

10 In power generation and aero-propulsion sectors,
superalloys, which are a class of structural alloys for
high temperature applications with excellent mechanical
properties and superior resistance to environmental
degradation, have been extensively developed and employed
15 in load-bearing hot section components of gas turbines.
However, due to the ever increasing demand to increase the
turbine inlet temperature for improved engine efficiency,
a materials system to effectively protect the hot section
components has been a critical requirement for current
20 generation combustion turbines. Extensive research efforts
over decades led to advanced protective coatings for
turbine components, primarily for thermal insulation, as
well as to enhance the oxidation/hot corrosion resistance
of turbine components.

25 Development of thermal barrier coatings has
undoubtedly been the most critical advancement in
materials technology for gas turbine applications. Thermal
barrier coatings are widely used in both industrial gas
turbine and aircraft engines. Thermal barrier coatings
30 facilitate a quantum leap in turbine inlet temperature (up
to 170°C) by providing thermal insulation to hot section
metallic components. Thermal barrier coatings, besides
facilitating such a tremendous increase in turbine inlet
temperature, also protect the load bearing structural

alloys of combustion turbines from extreme environment (high temperature, high pressure, corrosion) and have become the materials system of choice for improved efficiency and performance of gas turbine engines. These thermal barrier coating systems are usually made up of a triple layer structure, consisting of yttria-stabilized zirconia acting as the thermal barrier coatings; thermally grown oxide; and bond coat. Thermal barrier coating systems are highly employed for the use of protection from surrounding hot gases by temperature regulation and the prevention of oxidation and corrosion. A schematic drawing showing a typical thermal barrier coating system is provided in Fig. 1.

Among the various life-limiting factors, one key durability issue of thermal barrier coatings is their resistance to degradation due to air ingested calcium-magnesium-alumino silicate sand deposits. Thermal barrier coatings are increasingly susceptible to calcium-magnesium-alumino silicate attack which fills up voids in the thermal barrier coating layer. Due to the coefficient of thermal expansion mismatch between the super alloy and the thermal barrier coating layer, these voids are specially introduced into the thermal barrier coating layer to increase the strain tolerance and served as areas for stress relaxation. The ingestion of calcium-magnesium-alumino silicate into the thermal barrier coating layer during service fills up these voids, leading to the build-up of stress after many hours of service. This results in the formation of cracks, which agglomerate into delaminating, causing the eventual spallation and peeling off of the thermal barrier coating layer, which then exposes the underlying super alloy to the harsh environments. This is especially a problem in aircraft engines that operate in a dust-laden environment wherein

ingestion of siliceous debris into engines has been commonly reported. Similar to the contaminants due to fuel impurities, at elevated temperatures, these airborne deposits adhere, melt and degrade the thermal barrier coating system via a repeated freeze-thaw action and, to a certain extent, direct chemical reaction with thermal barrier coating constituents. The interactions that can accelerate the failure of thermal barrier coatings and underlying components include destabilization of the ceramic yttria-stabilized zirconia topcoat, accelerated oxidation and hot corrosion of the underlying metallic bond coat and superalloys.

Thus in order to protect thermal barrier coatings from both thermomechanical and thermochemical degradation of molten deposits, melt ingression into the porous yttria-stabilized zirconia topcoat should be completely suppressed. However, currently, there is no practice or method for improving the performance of thermal barrier coating after it is coated on super alloy.

There is a need to provide a method of treating a thermal barrier coating that overcomes, or at least ameliorates, one or more of the disadvantages described above.

There is a need to provide a system for treating a thermal barrier coating.

Summary

According to a first aspect, there is provided a method for treating a substance having a thermal barrier coating in contact with an alloy substrate comprising the step of irradiating the thermal barrier coating while the alloy substrate is maintained at a substantially constant temperature.

Advantageously, the method may be able to substantially decrease the amount of particulate matter (such as calcium-magnesium-almino-silicate) penetration into the thermal barrier coating. This may extend the
5 useful lifetime and reduce the service and maintenance costs for coated parts. In addition, the structure of the thermal barrier coating may not change significantly after irradiation treatment. The thermal barrier layer may not suffer from cracks.

10 Advantageously, the method may ensure uniform heating of the thermal barrier coating layer only, without heating the underlying alloy substrate portion. This can avoid overheating of the underlying alloy substrate and thereby prevent reduction in its mechanical and thermal
15 properties.

Advantageously, the method may be able to selectively heat up the thermal barrier coating only.

Advantageously, the method may increase the hardness of the thermal barrier coating.

20 Advantageously, the method may increase the density of the thermal barrier coating. This may result in a graded density where the thermal barrier coating is denser than the underlying layer (such as the thermally grown oxide layer or the bond coat). This may avoid the need to
25 employ an additional step of depositing a denser thermal barrier coating on top of a porous one which could be complicated and possess a larger coefficient of thermal expansion mismatch and lower strain tolerance due to the denser structure. This leads to a decrease in the time and
30 temperature required for densification of the thermal barrier coating as compared to conventional furnace annealing.

According to a second aspect, there is provided a system for treating a substance having a thermal barrier

coating in contact with an alloy substrate, the system comprising an enclosed chamber for receiving the substance, the enclosed chamber comprising heating means and radiation generating components.

5 Advantageously, the system may allow for selective heating of the thermal barrier coating only. In the system, both the underlying alloy substrate portion and the thermal barrier coating may be heated to different temperatures accordingly to match their coefficient of
10 thermal expansion mismatch as only the thermal barrier coating is affected by radiation while the alloy substrate portion is not. Hence, this may ensure that the stress due to coefficient of thermal expansion mismatch between the thermal barrier coating and alloy substrate is minimized.

15 According to a third aspect, there is provided a substance comprising an alloy substrate in contact with a radiation treated thermal barrier coating.

 Advantageously, the quality of the thermal barrier coating may be enhanced to substantially resist
20 penetration of particulate matter such as calcium-magnesium-alumino-silicate particles.

 Advantageously, the hardness of the thermal barrier coating may be higher than a conventional thermal barrier coating that is not subjected to radiation treatment.

25 Advantageously, the density of the thermal barrier coating may be higher (that is, less porous) than a conventional thermal barrier coating that is not subjected to radiation treatment.

Definitions

The following words and terms used herein shall have the meaning indicated:

The terms "contact", "contacting", or grammatical
5 variants thereof, when referring to the interaction
between a first substance and a second substance can refer
to a direct contact (in which the first substance is
physically in contact with the second substance without
any intervening layer) or can refer to an indirect contact
10 (in which the first substance is not physically in contact
with the second substance due to the presence of an
intervening layer(s) between the first substance and the
second substance). Where the first substance is an alloy
substrate and the second substance is a thermal barrier
15 coating, the intervening layer(s) between the alloy
substrate and the thermal barrier coating can include one
or more of a bond coat or a thermally grown oxide layer.
Where the first substance is a microwave absorber, the
microwave absorber can be in contact with a thermal
20 barrier coating (now the second substance).

The term "radiation source" is to be interpreted
broadly to include any electromagnetic waves that are
capable of heating a substance. Hence, the terms
"irradiating", "radiating", or grammatical variants
25 thereof, refer to a process of subjecting electromagnetic
waves to a substance, leading to the absorption of
electromagnetic waves which are then converted to thermal
energy.

The phrase "substantially constant temperature" is to
30 be interpreted broadly to refer to a temperature that does
not deviate significantly from a set value along the
course of time. Minor deviations from the set value (such
as up to 5% of the set value) as well as fluctuations
above or below the set value are permissible such that the

general trend of the temperature can be viewed as stable in the vicinity of or at the set value.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the
5 generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

10 Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a method for treating a substance having a thermal barrier coating in contact with an alloy substrate will now be disclosed.

The method comprises the step of irradiating the
15 thermal barrier coating while the alloy substrate is maintained at a substantially constant temperature.

The method may increase the resistance of the thermal barrier coating to ingress or penetration by particulate matter. Hence, the method may include a method for
20 increasing the resistance of a thermal barrier coating to ingress or penetration by particulate matter.

The method may increase the hardness of the thermal barrier coating. Hence, the method may include a method for increasing the hardness of a thermal barrier coating.

25 The method may decrease the porosity of the thermal barrier coating. Hence, the method may include a method for decreasing the porosity of a thermal barrier coating. Conversely, the method may include a method for increasing the density of a thermal barrier coating.

30 The thermal barrier coating may comprise any chemical composition known in the art for thermal barrier coatings. These include various ceramic materials such as zirconia (ZrO_2), yttria (Y_2O_3 , yttrium oxide), magnesia (MgO , magnesium oxide), ceria (CeO_2 , cerium oxide), In_2O_3 (indium

oxide, india), La_2O_3 (lanthanum oxide, lanthana), Pr_2O_3 (praesodymium oxide, praesodymia), Nd_2O_3 (neodymium oxide, neodymia), Sm_2O_3 (samarium oxide, samaria), Eu_2O_3 (europium oxide, europa), Gd_2O_3 (gadolinium oxide, gadolinia), Tb_2O_3 (terbium oxide, terbia), Dy_2O_3 (dysprosium oxide, dysprosia), Ho_2O_3 (holmium oxide, holmia), Er_2O_3 (erbium oxide, erbia), Tm_2O_3 (thulium oxide, thulia), Yb_2O_3 (ytterbium oxide, ytterbia), Lu_2O_3 (lutetium oxide, lutetia), Sc_2O_3 (scandium oxide, scandia), MgO (magnesium oxide, magnesia), CaO (calcium oxide, calcia), TiO_2 (titanium dioxide, titania), Ta_2O_5 (tantalum pentoxide, tantala) and combinations comprising at least one of the foregoing ceramic materials.

The thermal barrier coating may comprise zirconias stabilized by a metal oxide selected from yttria, dysprosia, erbia, europa, gadolinia, neodymia, praseodymia, urania, and hafnia and combinations thereof. The thermal barrier coating may comprise an yttria-stabilized-zirconia wherein the yttria is in an amount of six to eight weight percent yttria based on the total weight of the yttria-stabilized-zirconia. The yttria-stabilized-zirconia may be 7YSZ, which has high temperature durability, low thermal conductivity, and relative ease of deposition. The composition of the thermal barrier coating may affect the uptake of the electromagnetic waves during irradiation.

The alloy substrate may be a nickel, cobalt, titanium, aluminium and/or iron based alloy. The alloy may be a high temperature super alloy. Exemplary super alloys may be selected from the group consisting of Hastelloy, Inconel (for example IN100, IN600, IN713), PWA 1480, Waspaloy, Rene alloys (for example Rene 41, Rene 80, Rene 95, Rene N5), Haynes alloys, Incoloy, MP98T, TMS alloys,

Nimonic 80A and CMSX (for example CMSX-4 or CMSX-2) single crystal alloys.

The thermal barrier coating may be in direct contact with the alloy substrate. The thermal barrier coating may be in indirect contact with the alloy substrate such that there is at least one intervening layer between the thermal barrier coating and the alloy substrate. The intervening layer may include a thermally grown oxide layer and/or a bond coat. The thermally grown oxide layer may be due to the oxidation of the bond coat and may include oxides of aluminium, nickel chromium, magnesium, or combinations thereof. Hence, the thermally grown oxide layer may comprise Al_2O_3 , $\text{Ni}(\text{Al},\text{Cr})_2\text{O}_4$, NiO , $(\text{Cr},\text{Al})_2\text{O}_3$ or MgAl_2O_4 . The thermally grown oxide layer may be a single layer or multi-layer. The bond coat may comprise any composition known in the art for adhering a thermal barrier coating to an alloy substrate. The bond coat may comprise metallic oxidation-resistant materials such as MCrAlY alloy powders, where M represents a metal such as iron, nickel, platinum or cobalt. M may be various metal aluminides such as nickel aluminide and platinum aluminide.

The thermal barrier coating may be a combination of a pure thermal barrier coating of a percentage thereof comprising a metallic component in the form of a MCrAlY ranging from 0 to 50%.

The thermal barrier coating and bond coat, if present, may comprise one or more layers formed by known coating methods that include, but are not limited to plasma spraying (for example, air plasma spraying or vacuum plasma spraying), or other thermal spraying deposition methods (for example, high velocity oxy-fuel spraying, detonation spraying, or wire spraying), chemical

vapor deposition, or physical vapor deposition (for example electron beam physical vapor deposition).

The thermal barrier coating and bond coat, if present, may have any thickness. Exemplary thickness of
5 the thermal barrier coating may be selected from about 0.004 to about 0.200 inches. The bond coat may have a thickness in the range of from about 25 to about 495 micrometers (about 1 to about 19.5 mils). Bond coats deposited by physical vapour deposition techniques such as
10 electron beam physical vapor deposition may have a thickness in the range of about 25 to about 76 micrometers (about 1 to about 3 mils). Bond coats deposited by plasma spray techniques such as air plasma spraying may have a thickness in the range of from about 76 to about 381
15 micrometers (about 3 to about 15 mils). The thickness of the thermal barrier coating may affect the uptake of electromagnetic waves.

The porosity of the thermal barrier coating (before irradiation) may be at least about 2% to about 20%, about
20 2% to about 5%, about 2% to about 10%, about 2% to about 15%, about 5% to about 20%, about 10% to about 20%, about 15% to about 20%, or about 15% (measured using optical microscopy). The porosity of the thermal barrier coating may affect the uptake of electromagnetic waves.

25 The thermal barrier coating may be irradiated with electromagnetic waves such as radio waves, microwaves, infrared, ultraviolet, X-rays or gamma rays. The electromagnetic wave may be microwaves. The two main mechanisms of microwave heating are dipolar polarization
30 and conduction mechanism. Dipolar polarization is a process by which heat is generated in polar molecules. When an electromagnetic field is applied, the oscillating nature of the electromagnetic field results in the movement of the polar molecules as they try to align in

phase with the field. However, the inter-molecular forces experienced by the polar molecules effectively prevent such alignment, resulting in the random movement of the polar molecules and generating heat. Conduction mechanisms
5 result in the generation of heat due to resistance to an electric current. The oscillating nature of the electromagnetic field causes oscillation of the electrons or ions in a conductor such that an electric current is generated. The internal resistance faced by the electric
10 current results in the generation of heat. Accordingly, the microwaves may be used to produce high temperatures uniformly inside a material as compared to conventional heating means which may result in heating only the external surfaces of a material.

15 The microwaves may be applied at a power in the range of about 30 W to about 180 kW, about 30 W to about 150 kW, about 30 W to about 120 kW, about 30 W to about 100 kW, about 30 W to about 50 kW, about 30 W to about 25 kW, about 30 W to about 15 kW, about 30 W to about 10 kW,
20 about 30 W to about 5 kW, about 30 W to about 2 kW, about 30 W to about 1200 W, about 50 W to about 180 KW, about 2kW to about 180 KW, about 5kW to about 180 KW, about 10 kW to about 180 KW, about 15kW to about 180 KW, about 25kW to about 180 KW, about 50kW to about 180 KW, about 100kW
25 to about 180 KW, about 120kW to about 180 KW or about 150kW to about 180 KW.

Typical frequencies of microwaves may be in the range of about 300 MHz to about 300 GHz. This range may be divided into the ultra-high frequency range of 0.3 to 3
30 GHz, the super high frequency range of 3 to 30 GHz and the extremely high frequency range of 30 to 300 GHz. Common sources of microwaves are microwave ovens that emit microwave radiation at a frequency of about 0.915, 2.45, or 5.8 GHz. The microwaves may be applied with a

frequency in the range selected from the group consisting of about 0.3 GHz to about 300 GHz, about 0.3 GHz to about 200 GHz, about 0.3 GHz to about 100 GHz, about 0.3 GHz to about 50 GHz, about 0.3 GHz to about 10 GHz, about 0.3 GHz to about 5.8 GHz, about 0.3 GHz to about 2.45 GHz, about 0.3 GHz to about 0.915 GHz or about 0.3 GHz to about 0.9 GHz.

The microwave heating may be conducted for a period of time that is dependent on the composition and thickness of the thermal barrier coating. The time may be in the range of about 1 minute to about 5 hours, about 15 minutes to about 5 hours, about 30 minutes to about 5 hours, about 1 hour to about 5 hours, about 2 hours to about 5 hours, about 3 hours to about 5 hours, about 4 hours to about 5 hours, about 1 minute to about 15 minutes, about 1 minute to about 30 minutes, about 1 minute to about 1 hour, about 1 minute to about 2 hours, about 1 minute to about 3 hours or about 1 minute to about 4 hours.

The microwave heating may be carried out at a pulse repetition frequency where the pulses per second is in the range of about 10 to about 200, about 10 to about 50, about 10 to about 100, about 10 to about 150, about 50 to about 200, about 100 to about 200, or about 150 to about 200.

The microwave heating may be carried out at a temperature in the range of about 25°C to about 1500°C, about 25°C to about 50°C, about 25°C to about 100°C, about 25°C to about 250°C, about 25°C to about 500°C, about 25°C to about 750°C, about 25°C to about 1000°C, about 25°C to about 1250°C, about 50°C to about 1500°C, about 100°C to about 1500°C, about 250°C to about 1500°C, about 500°C to about 1500°C, about 750°C to about 1500°C, about 1000°C to about 1500°C or about 1250°C to about 1500°C.

The method may comprise the step of contacting the thermal barrier coating with a microwave absorber. The microwave absorber may be a high temperature material. The microwave absorber may be a carbon-based absorber or composites thereof. The microwave absorber may be selected from silicon carbide (SiC, including Al₂O₃-SiC, MgO-SiC, AlN-SiC or BeO-SiC), carbon black, activated carbon, carbon nanotubes, carbon nanofibers or multiwall carbon nanotube (MWCNT). The microwave absorber may be placed in contact with the thermal barrier coating such that the heated up microwave absorber can heat up the thermal barrier layer efficiently. Hence, the microwave absorber may aid in increasing the uptake of electromagnetic waves such as microwave by the thermal barrier coating.

Alternatively or concurrently with the use of a microwave absorber, in order to increase the uptake of electromagnetic waves by the thermal barrier coating, higher frequency, higher temperature or higher power of radiation may also be used.

The method may comprise the step of the alloy substrate in a receptacle that is a thermal insulator. The thermal insulator may be selected from the group consisting of ceramics, glass and plastics (such as polyethylene terephthalate (PET), high density polyethylene (HDPE), low density polyethylene (LDPE) or polypropylene). The receptacle may aid in reducing conduction losses through the alloy substrate so that the thermal barrier layer can be heated up efficiently. The receptacle may isolate the alloy substrate to prevent charging and sparking. The receptacle may also aid to contain the electromagnetic waves within the receptacle.

The method may comprise the step of pre-heating the substance before the irradiating step. Hence, the alloy substrate may be pre-heated to a desired temperature and

kept at that temperature as the thermal barrier coating is irradiated. The alloy substrate may be placed in the receptacle to maintain the temperature of the alloy substrate at a substantially constant temperature (which is the pre-heating temperature). Hence, the alloy substrate and the thermal barrier coating may be kept at different temperatures during irradiation to match their coefficient of thermal expansions. This may aid in minimizing stress due to coefficient of thermal expansion mismatch.

The pre-heating temperature may be selected from about 25°C to about 900°C, about 25°C to about 50°C, about 25°C to about 75°C, about 25°C to about 100°C, about 25°C to about 300°C, about 25°C to about 500°C, about 25°C to about 700°C, about 50°C to about 900°C, about 75°C to about 900°C, about 100°C to about 900°C, about 300°C to about 900°C, about 500°C to about 900°C or about 700°C to about 900°C. Pre-heating may aid to remove water vapour so as to prevent charging and sparking. In addition, pre-heating may aid to enhance the uptake of electromagnetic waves by the thermal barrier coating.

Exemplary, non-limiting embodiments of a system for treating a substance having a thermal barrier coating in contact with an alloy substrate will now be disclosed.

The system comprises an enclosed chamber for receiving the substance, the enclosed chamber comprising heating means and radiation generating components.

The system further comprises a receptacle for receiving the substance. The receptacle may be a thermal insulator as mentioned above.

The heating means of the system may pre-heat the enclosed chamber and/or substance to a desired temperature, as mentioned above.

The radiation generating components may be a magnetron tube for generating electromagnetic waves such as microwaves.

Exemplary, non-limiting embodiments of a substance
5 will now be disclosed.

The substance comprises an alloy substrate in contact with a radiation treated thermal barrier coating.

The thermal barrier coating of the substance may have a hardness of more than 5 GPa. The hardness of the thermal
10 barrier coating of the substance may be selected from the range of about 5 to about 10 GPa, about 5.5 to about 8.5 GPa, or about 6 to about 9 GPa.

The thermal barrier coating of the substance may have a surface that is substantially resistant to ingress of
15 particulate matter. The particulate matter may be calcium-magnesium-alumino-silicate particles.

The thermal barrier coating of the substance may have a porosity that is less than 15%, or less than 12%, less
20 than 11%, less than 10%, less than 9%, or about 9% to about 11%.

Hence, by irradiating the thermal barrier coating, it may have an improvement in one or more properties such as improved hardness, increased resistance to ingress or
25 penetration of particulate matter or decreased porosity.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however,
30 that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1 is a schematic diagram showing different sections of a typical thermal barrier coating system and

the temperature drop across the turbine blade to the thermal barrier coating.

Fig. 2a is a photograph showing the side view of a hybrid microwave furnace used in the Examples below. Fig. 2b is a photograph showing a top view of the experimental setup.

Fig. 3 is a graph showing the coefficient of thermal expansion values as a function of temperature for the various layers present in a thermal barrier coating system.

Fig. 4a is a scanning electron microscopy (SEM) image at a scale of 100 μm showing a typical thermal barrier coating layer acting as the control. Fig. 4b is a SEM image at a scale of 100 μm showing the microwave treated thermal barrier coating layer of Example 1.

Fig. 5a is a graph showing the modulus of the thermal barrier coating layer before and after microwave treatment. Fig. 5b is a graph showing the hardness of the thermal barrier coating layer before and after microwave treatment.

Fig. 6 is a series of energy dispersive X-ray spectroscopy mapping of untreated (A) and microwave treated thermal barrier coating samples at 1000°C for 1 hour (B), 1000°C for 2 hours (C) and at 1200°C for 1 hour (D).

Fig. 7 is a series of SEM images showing the microstructures of the untreated (A) and thermally treated (B) super alloy processed according to Comparative Example 1.

Fig. 8 is a graph showing the modulus of samples thermally treated at 500°C, 700°C and 900°C. The circled data showed that the modulus decreased at the temperature of 900°C.

Examples

A non-limiting example of the invention and a comparative example will be further described in greater detail, which should not be construed as in any way limiting the scope of the invention.

Example 1

As received super alloy substrates with precoated thermal barrier coatings (having a thickness of about 300 μ m measured using scanning electron microscopy and a porosity of about 15% measured using optical microscopy) were subjected to microwave treatment in a hybrid microwave furnace operating at 2.45GHz to modify their near surface properties. The super alloy substrate is an original Base Material Hastelloy X material coated with 8% Yittria Stabilised-Zirconia as the thermal barrier coating. Fig. 2a is a photograph showing the side view of the hybrid microwave furnace while Fig. 2b is another photograph showing the top view of the experimental setup.

Here, the super alloy substrate with the precoated thermal barrier coating was placed inside a ceramic crucible and covered with a piece of silicon carbide. The ceramic crucible reduced conduction losses through the metallic super alloy so that the thermal barrier coating can be heated up efficiently. In addition, the ceramic crucible functioned to isolate the metallic super alloy from the microwaves to prevent charging and sparking.

The silicon carbide functions as a good and efficient microwave absorber to allow for efficient heating up of the thermal barrier coating layer. Silicon carbide was chosen because it is a high temperature material which does not diffuse easily. By placing the silicon carbide on top of the thermal barrier coating layer, the heated up

silicon carbide can be used to heat up the underlying thermal barrier coating layer. This then mitigates the conduction losses through the super alloy substrate.

The hybrid microwave furnace consists of heating elements and microwave generating components. The heating elements heat up the furnace (as well as the sample) to remove water vapour in order to prevent charging and sparking as well as enhance the uptake of the microwaves in the thermal barrier coating layer.

The furnace is then maintained at an elevated temperature of about 900°C. Microwave power is then applied to heat the thermal barrier coating at a temperature of 1100°C for 2 hours.

In order to determine the microwave power to be applied, a few factors should be considered. These factors include the (i) coefficient of thermal expansion difference between the thermal barrier coating layer and the underlying multilayers (in particular that of the super alloy); (ii) the compositions of the thermal barrier layer and/or multilayer as this will result in different properties and coefficient of thermal expansion values, with different uptake of microwaves; and (iii) the thickness and porosity of the thermal barrier coating layer. Fig. 3 is a representative graph (obtained from Sheffler, K. D. and Gupta, D. K. (1988) Current status and future trends in turbine application of thermal barrier coatings. *J. Eng. Gas Turbines Power*, 110, 605) showing typical data for the coefficient of thermal expansion as a function of temperature for the various layers present in a thermal barrier coating system. Due to the coefficient of thermal expansion mismatch between the super alloy and the thermal barrier coating, specially designed void structures were introduced into the thermal barrier layer

to increase the strain tolerance (as can be seen in Fig. 4a).

The microwave treated thermal barrier coating sample was then characterized by SEM, modulus and hardness determination and thermal cycling.

Fig. 4a is a SEM image showing a control (untreated) thermal barrier coating layer with homogeneous distribution of splats and pores while Fig. 4b is a SEM image showing the microwave treated thermal barrier coating layer in which a denser thermal barrier coating layer was stacked on top of a less dense one. YSZ refers to yttria-stabilized zirconia, TGO refers to thermally grown oxide and BC refers to bond coat. This showed that there was a change in the porosity in the thermal barrier coating after the microwave treatment. The porosity of the microwave thermal barrier coating layer was about 9% to about 11%.

Fig. 5a shows the modulus of the thermal barrier coating layer before and after microwave treatment while Fig. 5b shows the hardness of the thermal barrier coating layer before (where the hardness is 4.6 GPa) and after (where the hardness is about 5.5 to about 8.5 GPa) microwave treatment. Upon microwave heat treatment, the modulus and hardness of the thermal barrier coating layer increased. The modulus and hardness also increased with increasing treatment temperature and time. Comparing Fig. 4a and Fig. 4b with Fig. 5a, it can be seen that the change in the porosity of the microwave treated thermal barrier coating sample did not affect the modulus significantly. Thus, it can be assumed that the amount of strain tolerance remains similar.

The untreated and microwave treated samples were then subjected to thermal cycling for 10 cycles at 1200°C with each cycle lasting 1.5 hours. Energy-dispersive X-ray

spectroscopy mapping of the thermal barrier coating layers of both the untreated and microwave treated samples are displayed in Fig. 6. Comparisons show that more calcium-magnesium-alumino silicate penetrated into the thermal barrier coating layer for the untreated thermal barrier coating sample as indicated by the amount of calcium-magnesium-alumino silicate still present on the top surface of the thermal barrier coating layer. Increases in the microwave treatment time or temperature reduced the amount of penetration as indicated by the increase in the amount of calcium-magnesium-alumino silicate still present at the top surface of the thermal barrier coating layer for the microwave treated sample.

Comparative Example 1

In this comparative example, a conventional furnace was used to thermally treat a sample having both the thermal barrier coating layer and the underlying super alloy substrate as those in Example 1. The heating temperature used was 900°C. This led to a change in the microstructure of the superalloy as shown in Fig. 7 and Fig. 8, which resulted in additional stress. Fig. 7 shows the morphologies of the control and thermally treated nickel superalloy. The thermally treated nickel superalloy had more crystallized structure as well as lower modulus values. This will reduce its mechanical and thermal performance and will affect its service life significantly. Fig. 8 shows the modulus of samples heated to 500°C, 700°C and 900°C. A decrease in the modulus accompanied a change in the microstructure at the heating temperature of 900°C.

Different layers such as the thermal barrier coating layer and the superalloy are made of different materials. Hence, they possess different properties such as different

coefficient of thermal expansion values. The use of a conventional furnace would heat up both the thermal barrier coating layer and the underlying superalloy substrate. In addition to the stress from the change in the microstructure of the superalloy substrate, additional stress are present due to the coefficient of thermal expansion mismatch between the superalloy and the thermal barrier coating layer when both layers are cooled after heating up to the same temperature inside the conventional furnace. Hence, it is shown that mere thermal treatment suffers from a number of disadvantages.

Applications

The disclosed method may be used to treat thermal barrier coatings for turbines, engines and related parts such as aircraft gas turbines, industrial gas turbines, turbine blades, turbine vanes, high pressure turbine duct segment, combustion engine, rocket engine, rocket engine parts, combustors and high pressure shrouds.

The disclosed method may decrease the amount of calcium-magnesium-alumino silicate penetration into a treated thermal barrier coating. This may aid in improving the hardness of the coating and extend the useful lifetime with reduction in service and maintenance costs.

The structure of the thermal barrier coating may not change significantly after microwave treatment. The disclosed method may ensure that the thermal barrier coating is heated up uniformly without heating the super alloy substrate. The disclosed method may result in selective heating of the coating since it is possible to selectively heat the coating to a temperature that is different from that on the super alloy substrate. This may ensure that the stress due to coefficient of thermal expansion mismatch between the layers is minimized.

In addition, the disclosed method may cause densification of the coating to a desired thickness or may be used to produce a graded density in the coating. Hence, this may avoid the need for an additional step of
5 depositing a denser thermal barrier coating layer on top of a porous one, which can be complicated and possesses a larger coefficient of thermal expansion mismatch and lower strain tolerance due to the denser structure.

The disclosed method may result in decreased time and
10 temperature required for densification of the coating as compared to conventional furnace heating. This may lead to savings in cost.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the
15 person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

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Claims

1. A method for treating a substance having a thermal barrier coating in contact with an alloy substrate comprising the step of irradiating said thermal barrier coating while said alloy substrate is maintained at a substantially constant temperature.

2. The method of claim 1, comprising the step of contacting said thermal barrier coating with a microwave absorber.

3. The method of claim 2, wherein said microwave absorber is a carbon-based absorber or composites thereof.

4. The method of any one of the preceding claims, comprising the step of placing said alloy substrate in a receptacle that is a thermal insulator.

5. The method of claim 4, wherein said thermal insulator is selected from the group consisting of ceramics, glass and plastics.

6. The method of any one of the preceding claims, comprising, before said irradiating step, the step of pre-heating said substance.

7. The method of claim 6, wherein said pre-heating step is undertaken at a temperature in the range of 25°C to 900°C.

8. The method of any one of the preceding claims, wherein said irradiating step is undertaken at a temperature in the range of 25°C to 1500°C.

9. The method of any one of the preceding claims, wherein said irradiating step is undertaken for a time period in the range of 1 minute to 5 hours.

5 10. The method of any one of the preceding claims, wherein said irradiating step is undertaken at a frequency in the range of about 0.3 GHz to about 300 GHz.

10 11. The method of any one of the preceding claims, wherein said irradiating step is undertaken at a pulse repetition frequency where the pulses per second is in the range of 10 to 200.

15 12. A system for treating a substance having a thermal barrier coating in contact with an alloy substrate, the system comprising an enclosed chamber for receiving said substance, said enclosed chamber comprising heating means and radiation generating components.

20 13. The system of claim 12, further comprising a receptacle for receiving said substance.

25 14. The system of claim 13, wherein said receptacle is a thermal insulator.

15. The system of any one of claims 12 to 14, wherein said heating means pre-heat said substance to a desired temperature.

30 16. The system of any one of claims 12 to 15, wherein said radiation generating component is a magnetron tube for generating microwaves.

35 17. A substance comprising an alloy substrate in contact with a radiation treated thermal barrier coating.

18. The substance of claim 17, wherein said thermal barrier coating has a hardness of more than 5 GPa.

19. The substance of claim 17 or 18, wherein said thermal barrier coating has a surface that is substantially resistant to ingress of particulate matter.

20. The substance of claim 19, wherein said particulate matter is calcium-magnesium-alumino-silicate particles.

21. The substance of any one of claims 17 to 20, wherein the porosity of said thermal barrier coating is less than 15%.