CVD ALUMINIDING PROCESS FOR PRODUCING A MODIFIED PLATINUM ALUMINIDE BOND COAT FOR IMPROVED HIGH TEMPERATURE PERFORMANCE

Inventors: Bangalore A. Nagaraj, West Chester, OH (US); Jeffrey L. Williams, Cincinnati, OH (US)

Assignee: General Electric Company, Schenectady, NY (US)

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ABSTRACT

A method of depositing by chemical vapor deposition a modified platinum aluminide diffusion coating onto a superalloy substrate comprising the steps of applying a layer of a platinum group metal to the superalloy substrate; passing an externally generated aluminum halide gas through an internal gas generator which is integral with a retort, the internal gas generator generating a modified halide gas; and co-depositing aluminum and modifier onto the superalloy substrate. In one form, the modified halide gas is hafnium chloride and the modifier is hafnium with the modified platinum aluminide bond coat comprising a single phase additive layer of platinum aluminide with at least about 0.5 percent hafnium by weight percent and about 1 to about 15 weight percent of hafnium in the boundary between a diffusion layer and the additive layer. The bond coat produced by this method is also claimed.

16 Claims, 1 Drawing Sheet
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The invention herein described was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

FIELD OF THE INVENTION

This invention relates generally to components of the hot section of gas turbine engines, and in particular, to a CVD aluminiding process for producing a modified platinum aluminate bond coat for improved high temperature performance.

BACKGROUND OF THE INVENTION

In gas turbine engines, for example, aircraft engines, air is drawn into the front of the engine, compressed by a shaft-mounted rotary compressor, and mixed with fuel. The mixture is burned, and the hot exhaust gases are passed through a turbine mounted on a shaft. The flow of gas turns the turbine, which turns the shaft and drives the compressor. The hot exhaust gases flow from the back of the engine, providing thrust that propels the aircraft forward.

During operation of gas turbine engines, the temperatures of combustion gases may exceed 3,000°F, considerably higher than the melting temperatures of the metal parts of the engine, which are in contact with these gases. The metal parts that are particularly subject to high temperatures, and thus require particular attention with respect to cooling, are the hot section components exposed to the combustion gases, such as blades and vanes used to direct the flow of the hot gases, as well as other components such as shrouds and combustors.

The hotter the exhaust gases, the more efficient is the operation of the jet engine. There is thus an incentive to raise the exhaust gas temperature. However, the maximum temperature of the exhaust gases is normally limited by the materials used to fabricate the hot section components of the turbine. In current engines, hot section components such as the turbine vanes and blades are made of cobalt-based and nickel-based superalloys, and can operate at temperatures of up to 2000°F to 2300°F.

The metal temperatures can be maintained below melting levels with current cooling techniques by using a combination of improved cooling designs and thermal barrier coatings. In one approach, a thermal barrier coating system is applied to the metallic turbine component, which becomes the substrate. The thermal barrier coating system includes a ceramic thermal barrier coating that is applied to the external surface of metal parts within engines to impede the transfer of heat from hot combustion gases to the metal parts, thus insulating the component from the hot exhaust gas. This permits the exhaust gas to be hotter than would otherwise be possible with the particular material and fabrication process of the component.

Thermal barrier coatings (TBCs) are well-known ceramic coatings, for example, yttrium stabilized zirconia. Ceramic thermal barrier coatings usually do not adhere optimally directly to the superalloys used in the substrates. Therefore, an additional metallic layer called a bond coat is placed for example, by chemical vapor deposition (CVD), between the substrate and the TBC to improve adhesion of the TBC to the underlying component. In one form, the bond coat is made of a diffusion nickel aluminate or platinum aluminate, whose surface oxidizes to form a protective aluminum oxide scale in addition to improving adherence of the ceramic TBC.

The bond coat temperature is critical to the life of the TBC and has been limited to about 2100°F. Once the bond coat exceeds this temperature, the coating system can quickly deteriorate, resulting in separation of the TBC from the bond coat. The addition of small amounts of reactive elements to platinum aluminate coatings, such as Hf, Si, Zr, and Y have been shown to improve performance of such coatings.

U.S. Pat. No. 5,658,614 to Basta et al. discloses a method of improving the oxidation resistance of a platinum modified aluminate coating applied to a nickel based superalloy substrate. In one embodiment, a hafnium-modified aluminate coating was formed using a coating gas mixture of aluminum trichloride, hydrogen and hafnium chloride. The first coating gas mixture was generated externally to a retort holding the platinum-plated workpiece that was to be coated by passing hydrogen and hydrogen chloride over a pure source of aluminum. A second mixture of Ar and HCl was generated in a separate generator external to the retort that also contained a pure hafnium bed, thereby forming hafnium chloride. The mixtures were then introduced concurrently to the coating retort forming a hafnium modified outwardly grown, single phase aluminate coating, as the gases flowed over the workpiece, depositing Hf and Al.

U.S. Pat. No. 5,989,733 to Warnes et al. is directed to a CVD outwardly grown platinum aluminate diffusion coating on a nickel or cobalt based superalloy substrate wherein the platinum modified aluminate diffusion coating is modified to include a combination of hafnium and silicon in a concentration of about 0.01% by weight (w/o) to about 8 w/o of the outer additive layer of the coating. The coating gas mixture was generated externally by passing high purity hydrogen and high purity hydrogen chloride over a high purity pure source of aluminum and then passing the mixture over a high purity pure source of silicon, both sources at 290°C (554°F) and external of the retort. A mixture of Ar and HCl was flowed in an external chloride generator through a hafnium bed at 430°C (806°F). Both gas coating mixtures were then introduced concurrently to the retort.

Prior modified platinum aluminum bond coat practice, as exemplified by the foregoing U.S. patents, involves generating two or more distinct gas coating mixtures in multiple external gas generators and concurrently introducing these mixtures into the retort.

U.S. Pat. No. 5,667,663 to Rickerby et al. discloses a method for adhering a ceramic TBC layer to a superalloy article containing a predetermined amount of aluminum. After applying a layer of platinum to the superalloy article and heat treating the article, the aluminum diffuses from the superalloy article into the platinum. In one embodiment, hafnium is added to the platinum layer by chemical vapor deposition up to a level of 0.8 w/o. Deposition of the aluminum by CVD is not disclosed.

What is needed are improved methods to apply these reactive element modified diffusion bond coating systems. The present invention fulfills this need, and further provides related advantages.

SUMMARY OF THE INVENTION

In one form, the present invention provides both an improved method of producing coatings modified with reactive metals, such as hafnium-modified coatings and the...
coatings produced by that method, utilizing a single gas
generation system in a diffusion coating process. An external
system generates an aluminum halide gas which, as it is
flowed into the system, passes over the reactive metal
located between the external generator and the workpiece or
parts which are located within a coating retort, and prefer-
ably the reactive metal is within, the coating retort where the
parts to be coated are located. As used herein, reactive
metals include Zr, Hf, V, Nb, Ta, Y, La and Ce. The reactive
metal is activated by the aluminum halide gas to form a
mixture of aluminum halide gases and at least one reactive
metal halide gas species. In this manner, a reactive metal and
aluminum are co-deposited by an internal gas generation
method onto the parts to be coated as the gases pass over the
parts to produce a modified single phase additive layer of
platinum/aluminide.

In another form, the present invention comprises a chemi-
cal vapor deposited outwardly grown platinum aluminide
diffusion coating on a nickel or cobalt based superalloy
substrate wherein hafnium and aluminum are co-deposited
by an internal gas generation method onto the platinum-
plated parts to produce a single phase additive layer of
platinum aluminide with up to about 0.5 percent hafnium by
weight percent, and about 1 to about 15 weight percent of
hafnium in the boundary between the diffusion layer and the
additive layer.

In yet another embodiment, the present invention com-
prises a TBC system for application to a superalloy substrate
used in the hot section of a gas turbine engine. A layer of
a platinum group metal is first applied to the superalloy
substrate. A modified platinum aluminide diffusion coating
is formed by applying, by co-deposition, aluminum and at
least one reactive metal, such as hafnium, using chemical
deposition to the platinum group metal, the coating
comprising a single phase additive layer of platinum alumi-
minide with at least about 0.1 percent hafnium by weight
(w/o) and about 0.1 to about 15 weight percent (w/o) of
hafnium in the boundary formed by the diffusion layer
between the substrate and the additive layer, and a ceramic
thermal barrier coating applied to the modified platinum
aluminide diffusion coating. The amount in weight percent-
age of reactive metal will vary depending upon the species
selected.

While in the prior art, hafnium chloride and aluminum
chloride gas coating mixtures are separately generated exter-
nally then concurrently introduced into the retort causing the
hafnium and aluminum to precipitate out as they pass over
the workpiece, in the present invention, there is only one
external gas generator generating the gases bearing both the
reactive metal species and the aluminum. In the additive
layer, there is a relatively low concentration of the reactive
metal so that the reactive metal is in solution with the
platinum and aluminum.

One advantage of the present invention is that the coating
system produced by this invention demonstrates increased
service life resulting from improved spallation resistance of
the TBC system.

Another advantage of the present invention is that the
process consists of a single step that additionally coats the
internal and external surfaces of an article to be coated with
the modified platinum aluminum coating. This one step
process allows for cost savings during the manufacturing
process.

Still another advantage of the present invention is that the
internal gas generation process provides the capability for
the modification of existing CVD reactors to produce reac-
tive element-modified coatings without the addition of new
external gas generation systems.

Yet another advantage of the present invention is that the
process can be easily adapted for use in airfoil material
repair operations. It is advantageous to have the ability to
repair a damaged section of an airfoil, rather than having to
strip the entire TBC coating and completely re-bond and
re-coat a TBC coating to the entire part.

Another advantage of the present invention is that the
CVD coating device and process can be simplified as the
device of the present invention requires only one external
gas generator.

Continuing and often interrelated improvements in pro-
cesses and materials, such as the improvements of the
present invention, can provide cost reductions and major
increases in the performance of devices such as aircraft gas
turbine engines.

Other features and advantages of the present invention
will be apparent from the following more detailed descrip-
tion of the preferred embodiment, taken in conjunction
with the accompanying drawings which illustrate, by way of
example, the principles of the invention.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic of a CVD system of a version of the
present invention; and

FIG. 2 is a cross-section at A—A of the internal gas
generator of FIG. 1.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Referring now to the figures, where like parts have the
same numbers, in accordance with a preferred embodiment
of the invention, there is shown in FIG. 1 a schematic of a
CVD system of a version of the present invention.

Articles to be coated (not shown), for example, compo-
nents requiring environmental coatings and/or thermal bar-
rier coating systems were fixtured in a retort that appli-
ced a layer of platinum to the article using known methods,
for example, electroplating followed by an optional diffusion
heat treatment. When an optional diffusion heat treatment is
performed, a mixture of Pt and PtAl₃ and NiAl can be
produced. This optional diffusion layer can be grown into
the substrate as Al and Ni from the substrate diffuse out-
wardly. These components may be, for example, compo-
nents located in the hot section of a gas turbine engine, for
example, a jet engine, such as, for example, turbine blades
and vanes, combustors, shrouds and other such components.

An external generator 4 receiving a flow of gas from gas
inlets 6 was used to produce aluminum trichloride gas using
standard CVD processes well known in the art. A source of
halide gas is introduced into the external generator that
includes a source of aluminum. The generator is maintained
at an elevated temperature by a heat source to allow for the
formation of AlCl₃. The externally generated AlCl₃ gas was
passed through an internal gas generator 8. The internal
generator 8 was in the form of an array 20 of seven tubes 22
configured as shown in FIG. 2. To act as a fluid conduit from
the external generator to the retort 2 such that at least a
portion of the array was disposed within the retort 2 which
can also be heated to an elevated temperature by an inde-
pendent heat source in order to control the rate of deposition
of metal from gases as will be explained. The portion of the
tubes 22 disposed within the retort was perforated in a
manner and in a location that allowed active gas to be
The composition of the coating is also modified to include more than one reactive metal, if desired. For example, if it is desired that the composition of the coating includes several reactive metals, then these reactive metals can be added to the composition by including chips of these desired metals in one or more of the tubes shown in FIG. 2. For example, if it is desired that a coating include Nb and Ta in addition to Hf, then tubes in the internal generator can include chips of Hf, Ta and Nb, which can be converted to chloride-bearing species of each of these elements as the AlCl3 is passed over the metal chips. The desired partial pressure, and hence the amount of each reactive element in the coating, can be adjusted by controlling the amount of metal chips in the tubes. More tubes have additional amounts of these reactive metals added, or additional metals added to achieve both the desired composition and concentration in the coating.

Of course, following application of the additive layer in each of these examples, an optional heat treatment of from about 1 to about 4 hours at temperatures of from about 1800°F to about 2000°F (982-1093°C) is applied to allow for additional diffusion of elements from each of these elements into the diffusion layer as well as growth of the diffusion layer, and to allow elements such as Pt and Ni to diffuse into the additive layer, if desired, prior to application of a TBC. However, the optional heat treatment is not necessary, since sufficient diffusion occurs while the substrate is within the retort during CVD processing. Because the CVD process is applied at temperatures between 1800°F-2200°F (982-1204°C) for periods of time of 1-4 hours, there is sufficient time at elevated temperatures for diffusion to occur and for a diffusion layer to form between the additive layer and unaffected substrate.

The following two examples demonstrate that the hafnium-modified platinum aluminide bond coatings produced by the present invention resulted in significant furnace cycle test life improvements and hence, increased bond strength at 2125°F (1163°C).

A sample of 20 test coupons were prepared using a composition of Rene N5 superalloy, which nominally is 7.5 wt. % Co; 6.2 wt. % Al; 7 wt. % Cr; 6.5 wt. % Ta; 5 wt. % W; 1.5 wt. % Mo; 3 wt. % Re; 0.15 wt. % Hf; 0.5 wt. % max Y; 0.05 wt. % C; 63.1 wt. % Ni; and 40 ppm B. All samples had a layer of platinum applied utilizing electroplating followed by a heat treatment in the temperature range of about 1800°F-2000°F (982-1093°C) for about 1 to 4 hours as is well known in the art to produce a thickness of about 0.3 mils.

Three samples received a platinum aluminide bond coat using prior art chemical vapor deposition, to be used as a baseline.

**Example 1**

Nine test coupons were placed in a retort and heated to a temperature of about 1100°F (426°C). Utilizing the method of the present invention, three of the outer tubes of the internal gas generator of FIG. 2 were completely filled with hafnium chips. AlCl3 gas was delivered to the hafnium filled tubes of the internal gas generator from a prior art external Al gas generator at a temperature of about 450°C (842°F) and a flow rate of about 3 liters per minute (lpm). Hydrogen carrier gas was flowed through the center pipe at about 189 lpm, through the inactivated internal pipes (those without hafnium chips) at about 19 lpm, and through the active internal pipes (those containing the hafnium chips) at about 47 lpm for a total of about 480 minutes (not including warm-up/purge/shutdown).
Following application of the modified platinum aluminide bond coat according to the present invention, the nine test coupons and three baseline coupons were subjected to furnace cycle testing. Each cycle of the furnace cycle test consisted of heating the coupon to about 2125°F (1163°C) over a 10 minute period, maintaining the coupon at a temperature of about 2125°F (1163°C) for a period of about 45 minutes, and allowing the coupon to cool to a temperature of about 200°F (93°C) over a nine minute period. This cycle was repeated until there was bond failure.

The baseline coupons had an average furnace cycle test (FCT) life of 240 cycles, while the modified platinum aluminide bond coat of the present invention had an average FCT life of 818 cycles, clearly signifying an FCT life improvement (representing increased bond strength).

**EXAMPLE 2**

Eight test coupons were placed in a retort and heated to a temperature of about 1100° C. (2122°F). Utilizing the method of the present invention, three of the outer tubes of the internal gas generator of FIG. 2 were filled approximately three quarter full with hafnium chips. AlCl₃ gas was delivered to the hafnium filled tubes of the internal gas generator from a prior art external Al generator at a temperature of about 450°C (842°F) and a flow rate of about 3 liters per minute (lpm). Hydrogen carrier gas was flowed through the center pipe at about 189 lpm, through the inactive internal pipes (those without hafnium chips) at about 19 lpm, and through the active internal pipes (those containing the hafnium chips) at about 47 lpm for a total of about 480 minutes (not including warm-up/purge/shutdown).

Following application of the modified platinum aluminide bond coat according to the present invention, the eight test coupons and were subjected to furnace cycle testing as described in Example 1 and compared to the FCT life of the three baseline coupons described in Example 1.

The modified platinum aluminide bond coat had an average FCT life of 1008 cycles compared to the baseline 418 cycles, clearly signifying further improvement (representing further increased bond strength).

A major factor in arriving at the benefits of the present invention is that the aluminum and reactive metals such as hafnium are co-deposited in solution as a single phase in the additive layer utilizing only one external gas generator. It is believed that the processes of the present invention are also successfully applicable to cobalt based superalloy substrates.

A further advantage of the present invention is that the process provides the capability for modification of existing CVD reactors to produce hafnium-modified coatings or coatings including a plurality of reactive metals without the addition of new external gas generation systems.

Although the present invention has been described in connection with specific examples and embodiments, those skilled in the art will recognize that the present invention is capable of other variations and modifications within its scope. For example, although Hf modifier has been used as an exemplar, it is envisioned other reactive metal modifiers may be utilized individually in place of Hf or in combination with Hf and with themselves, as desired. These examples and embodiments are intended as typical of, rather than in any way limiting on, the scope of the present invention as presented in the appended claims.

**What is claimed is:**

1. A method of depositing a modified platinum aluminide diffusion coating onto a superalloy substrate, comprising the steps of:
   - applying a layer of a Pt-group metal over at least one surface of the superalloy substrate;
   - placing the Pt-group metal-coated superalloy substrate into a CVD retort;
   - generating an Al-halide gas in an external gas generator;
   - generating a modified reactive metal-halide gas by passing a portion of the Al-halide gas generated in the external gas generator into an internal gas generator, a portion of which extends into the retort and that includes at least one reactive metal to produce a modified reactive metal-halide gas;
   - mixing the Al-halide gas and the modified reactive metal-halide gas together;
   - passing the mixture of Al-halide gas and the reactive metal-halide gas over the Pt-group-plated, superalloy substrate in the retort for a preselected period of time at a preselected temperature and co-depositing Al and the reactive metal onto the Pt-group plated superalloy substrate to form a reactive metal-modified platinum group aluminide coating over the substrate.

2. The method of claim 1 wherein the step of generating a modified reactive metal-halide gas includes contacting a portion of the Al-halide gas with a gas generator that includes at least one reactive metal selected from the group consisting of Hf, Zr, Nb, Ta, Y, La and Ce.

3. The method of claim 1 wherein the step of generating a modified metal-halide gas is accomplished by passing the Al-halide gas through an internal gas generator.

4. The method of claim 1 wherein the internal gas generator is comprised of a plurality of tubes having at least one of which includes at least one reactive metal.

5. The method of claim 4 wherein the internal gas generator is comprised of seven tubes for transporting Al-halide gas from the external gas generator to the retort, at least one of the tubes including a source of at least one reactive metal for generating the modified reactive metal-halide gas.

6. The method of claim 1 further including the step of applying a ceramic thermal barrier coating over the reactive metal-modified Pt-group aluminide coating.

7. The method of claim 2 wherein the step of generating a modified reactive metal-halide gas includes passing a portion of the Al-halide gas into a gas generator that includes the reactive metal Hf.

8. The method of claim 7 wherein the step of co-depositing Al and the reactive metal includes co-depositing Hf and Al onto a Pt-plated superalloy substrate to form a Hf-modified platinum aluminide coating having a single phase additive layer of platinum aluminum having at least about 0.1 w/o Hf and a diffusion layer formed between the substrate and the additive layer, the diffusion layer having a variable amount of Hf from about 0.1 w/o to about 15 w/o, the balance of the diffusion layer comprising Al, Pt and Ni.

9. The method of claim 1 wherein the step of passing the mixture of Al-halide gas and the reactive metal-halide gas over the Pt-group-plated, superalloy substrate in the retort at a preselected temperature is performed for about one to four hours.

10. The method of claim 1 wherein the step of passing the mixture of Al-halide gas and the reactive metal-halide gas...
over the platinum group-plated, superalloy substrate in the retort for a preselected period of time is performed at a temperature in the range of from about 1800°-2200° F.

11. The method of claim 1 further including heat treating the Pt-group-metal coated superalloy substrate for period of about 1-4 hours at a temperature in the range of about 1800°-2000° F. to develop a diffusion zone between the deposited Pt-group metal and the substrate prior to placing the substrate into the retort.

12. The method of claim 2 wherein the step of generating a modified reactive metal-halide gas by passing a portion of the Al-halide gas generated in the external gas generator into the gas generator positioned in the retort between the substrate and the external gas generator.

13. A method of depositing a modified platinum aluminide diffusion coating onto at least one surface of a nickel-based superalloy substrate, comprising the steps of:
   - Electrodepositing a layer of Pt onto the superalloy substrate;
   - Placing the Pt-coated superalloy substrate into a CVD retort;
   - Forming an AlCl₃ gas by introducing a chlorine gas into an external gas generator and passing the gas over a source of Al at a temperature sufficient to form AlCl₃;
   - Passing a portion of the AlCl₃ over a source of Hf at a temperature sufficient to reduce AlCl₃ and generate a gas including a portion of HfCl₄;

mixing the AlCl₃ gas and the HfCl₄ together;
passing the mixture of AlCl₃ and the HfCl₄ gas together over the Pt-plated, superalloy substrate in the retort for a preselected period of time at a preselected temperature; and
co-depositing Al and Hf onto the Pt-plated superalloy substrate to form a Hf-modified platinum aluminide coating over the substrate.

14. The method of claim 13 wherein the step of co-depositing Al and Hf includes co-depositing onto the Pt-plated superalloy substrate to form a Hf-modified platinum aluminide coating having a single phase additive layer of platinum aluminide with at least about 0.1 w/o Hf in solution.

15. The method of claim 14 further including a diffusion layer formed between the substrate and the additive layer, the diffusion layer having a variable amount of Hf from about 0.1 w/o to about 15 w/o, the balance of the diffusion layer comprising Al, Pt and Ni.

16. The method of claim 13 wherein the step of passing the mixture of Al-halide gas and Hf-halide gas over the platinum group-plated, superalloy substrate in the retort for a preselected period of time is performed at a temperature in the range of from about 1800°-2200° F. for about one to four hours.