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(54) Titre : PROCEDE POUR L'APPLICATION D'UN SYSTEME DE REVETEMENT DE PROTECTION THERMIQUE SUR UN SUBJECTILE METALLIQUE
(54) Title: A PROCESS FOR APPLYING A HEAT SHIELDING COATING SYSTEM ON A METALLIC SUBSTRATE

(57) Abrégé/Abstract:
The invention provides a process for applying a heat shielding coating system on a metallic substrate. The coating system comprises at least three individual layers selected from the group of barrier layer, hot gas corrosion protection layer, protection layer, heat barrier layer, and smoothing layer. The coating system is applied to the metallic substrate by low pressure plasma spraying in a single operation cycle. This process enables the layers to be applied in an arbitrary sequence. The process is preferably used in applying a coating system to a turbine blade, particularly a stator or a rotor blade of a stationary gas turbine or of an aircraft engine, or to another component in a stationary or aircraft turbine that is subjected to hot gas.
Abstract of the Disclosure

The invention provides a process for applying a heat shielding coating system on a metallic substrate. The coating system comprises at least three individual layers selected from the group of barrier layer, hot gas corrosion protection layer, protection layer, heat barrier layer, and smoothing layer. The coating system is applied to the metallic substrate by low pressure plasma spraying in a single operation cycle. This process enables the layers to be applied in an arbitrary sequence. The process is preferably used in applying a coating system to a turbine blade, particularly a stator or a rotor blade of a stationary gas turbine or of an aircraft engine, or to another component in a stationary or aircraft turbine that is subjected to hot gas.
A PROCESS FOR APPLYING A HEAT SHIELDING COATING SYSTEM
ON A METALLIC SUBSTRATE

Background of the Invention

The most significant progress, as far as an increase in performance of machines like turbines are concerned, can be realized by increasing the process temperature. However, such increase in process temperature can result in the fact that metallic components of the machine are stressed beyond the limits of their safe operating area such that these components will not endure an operation under these conditions for a long time without damage or at least alteration of their properties.

It is well known in the prior art to make use of coatings applied to such metallic components in order to protect them from such critical operating conditions. For example, ceramic heat shield coats are used to decrease the heat conductivity between process chamber and machine component, or metallic coats to increase the hot gas corrosion resistance of the surface of such metallic machine components. For many years, such coats are also applied by a thermal coating process; nowadays, they are state of the art.
Since in most cases one single coat is not sufficient to resist a complex stress attack, particularly if the stress is extremely high, preferably a coating system consisting of a plurality of different layers is applied; thereby, each layer has specific properties particularly suitable to withstand a specific stress. A typical example is to apply a stabilized zirconium dioxide layer, serving as a heat shield layer, onto a metallic layer that is resistant against hot gas corrosion, for example a MCrAlY-layer, whereby M represents a metal on the basis of cobalt, nickel or iron. Preferably, such a layer is applied directly onto the component to be protected.

Following the requirements regarding performance and life span, in the past further layers have been developed to be applied in addition to the two-layer-systems "Stabilized Zirconium Oxide/MCrAlY". Since it can happen at high temperatures that a diffusion of important metal atoms occurs between the substrate and the MCrAlY-layer, the last named layer changes its properties in a negative sense until it cannot fulfill its function any longer. In order to prevent this side effect, an intermediate layer, located between the substrate and the MCrAlY-layer, has been developed, serving either as a diffusion barrier or as a donor of important metal atoms (designated in the following as "barrier layer"). A further intermediate layer is already used for the region between the MCrAlY-Layer and the barrier layer which reduces the oxidative
attack to the MCrAlY-layer and improves the adherence to the barrier layer.

Prior Art

U.S. Patent No. 5,238,753 discloses a thermal barrier coating system for high temperature superalloys that includes an intermetallic bond coating on the substrate, e.g. a metallic base body member for an aircraft jet engine turbine blade made of a Cr-Co-Fe-alloy or another alloy on the basis of Co and Ni, and a ceramic topcoat having a columnar grain structure with the columnar axis perpendicular to the surface of the coating. The intermetallic coating is preferably a nickel aluminide or a platinum aluminide, whose upper surface is oxidized during processing to form a thin layer of predominantly aluminum oxide. The ceramic topcoat is preferably zirconium oxide having from about 6 to 20 percent yttrium oxide. The ceramic topcoat is applied to the substrate by an EB-PVD method, i.e. Electron Beam Physical Vapor Deposition, whereby zirconium oxide or yttrium oxide is vaporized from a metallic body member by means of an electron beam gun.

Further methods and examples of applying a heat shield layer system onto a gas turbine blade are disclosed in U.S. Patents Nos. 5,514,482 and 4,409,659.

In U.S. Patents Nos. 4,321,310 and 4,321,311, heat shield layer systems are disclosed having a primer layer of the type
MCrAlY between the zirconium oxide layer and the metallic substrate. As a possible method of manufacturing a heat shield layer of zirconium oxide, a PVD method is suggested, i.e. method based on physical vapor deposition.

The German Patent Document A1-197 41 961 entitled "Ceramic Heat Insulating Coating of Columnar Structure" filed September 23, 1997 by Siemens AG suggests that it may be advantageous to provide for a chemical binding of the heat shield layer to the metallic primer layer in view of an increased life span and an improved adherence of the heat shield layer system to the substrate. This is realized for example by providing a thin layer of Al₂O₃. As a primer layer, as well a layer of a ternary Al-Zr-O compound may be used. The ternary Al-Zr-O compound, e.g. Al₂Zr₂O₇ is preferably used for binding a heat shield layer comprising zirconium oxide.

The heat shield layer preferably comprises a metallic substance, particularly zirconium oxide. This metal oxide is preferably alloyed with a stabilizer, e.g. yttrium oxide, to prevent a phase change at high temperatures. The zirconium oxide is alloyed preferably with 3 to 20% by weight, particularly with 8% by weight of yttrium oxide. Also other rare earth substances, like e.g. cerium oxide or scandium oxide, can be used as stabilizers for zirconium oxide.

All these layers are applied by partially very different methods, mainly in order to save costs: The barrier layers are for example galvanically applied; the hot gas corrosion protection
layer e.g. by means of LPPS (Low Pressure Plasma Spraying) or HVOF (High Velocity Oxygen Fuel); the protection layer e.g. by means of PVD (Physical Vapor Deposition); and the heat shield layer e.g. by means of APS (Atmospheric Plasma Spraying) or EB-PVD (Electron Beam Physical Vapor Deposition). It is understood that all these different application methods require the provision of a huge amount of available equipment for the different technologies, resulting in partially high manufacturing costs. A particular disadvantage in connection with the EB-PVD method is the extremely high investment required for the electron beam gun, for an apparatus to provide a high-vacuum, for the high-vacuum chamber and for the partial pressure control apparatus. Moreover, the capacities of the particular methods cannot be expanded to all layers. By means of the EB-PVD method, for example, the areas of a substrate that are not directly visible during the coating operation cannot be coated at all or only insufficiently. The more multifarious the choice of the different layers is made, the more complex the variety of the coating technologies will get.

Objects of the Invention

It is an object of the present invention to replace the plurality of different coating methods, that have been required for applying the different layers, by a single coating method.
Summary of the Invention

To meet this an other objects, the present invention provides a process for applying a heat shielding coating system on a metallic substrate. The coating system comprises at least three individual layers selected from the following group of layers:

- Barrier layer;
- Hot gas corrosion protection layer;
- Protection layer;
- Heat barrier layer;
- Smoothing layer;

The coating system is applied to the metallic substrate by low pressure plasma spraying in a single operation cycle.

In the following, the low pressure plasma spraying method (LPPS) is subdivided into the LPPS-Thick Film Method (conventional LPPS) and the LPPS-Thin Film Method (new LPPS according to U.S. Patent No. 5,853,815).

Up to now, the simplification of the manufacturing process reached by the present invention was not possible because the thickness of the particular layers was different from layer to layer, typically a few micrometers in the case of the intermediate layers up to a few millimeters in the case of the heat shield layers. By using the processes know in the past, either only a thin layer or only a thick layer could be applied to a substrate, due
both to technological and economical reasons. The U.S. Patent No. 5,853,815 discloses a LPPS-Thin Film Method that is fundamentally suitable to apply a heat shielding layer system of the kind referred to onto a metallic substrate.

In this LPPS-Thin Film Method, a plasma torch is created in an atmosphere of particularly low pressure. Compared to older LPPS-Thick Film Methods, a plasma torch results that is considerably enlarged in transversal direction and has a de-focusing effect on a powder jet injected into the plasma torch by means of a conveying gas. Within a period of time, considered short in the field of thermal coating processes, a great area can be treated with the plasma jet containing the dispersed coating material. By using such a LPPS-Thin Film Method, in which a plasma jet with a length of up to 2.5 meters is used, very thin an uniform layers of coating material can be applied to a substrate.

In order to develop a coating system having a well defined density, the coating system has to be built-up with a plurality of individual coat applications. A suitable coating material consists of a mixture of powder particles, the mean particle diameter preferably being less than 50 μm. Each and every individual particle whose diameter is not substantially greater than the afore mentioned mean diameter is partly or fully molten in the plasma jet, with the result that, upon the molten particles hitting the surface of a substrate, a coating layer is created having a well de-
fined density and thickness. The microscopic structure of the applied layer is adjustable, as far as its density and porosity, respectively, is concerned, by suitably selecting the spraying and powder parameters.

The application of the LPPS coating process for the creation of the entire layer system unveils for the first time the possibility to create both thin and thick layers without the need of changing the coating technology and/or equipment, as it has been required up to now.

The layer system as a whole can be heat treated after having been applied to a substrate.

The preferred parameters of the layers coming into consideration are summed up in the following table.
**TABLE**

<table>
<thead>
<tr>
<th>LAYER</th>
<th>MATERIAL</th>
<th>THICKNESS OF LAYER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrier Layer</td>
<td>Metallic, particularly metal alloy, preferably NiAl- or NiCr-Alloy</td>
<td>1 to 20μm, preferably 8 to 12μm</td>
</tr>
<tr>
<td>Hot Gas Corrosion Protection Layer</td>
<td>Metallic, particularly MCrAlY-Alloy (whereby M is Fe, Co or Ni), or Metal Aluminid</td>
<td>50 to 500μm, preferably 100 to 300μm</td>
</tr>
<tr>
<td>Protection Layer</td>
<td>Aluminum Oxide or Ternary Al-Zr-O-Alloy</td>
<td>1 to 20μm, preferably 8 to 12μm</td>
</tr>
<tr>
<td>Heat Shield Layer</td>
<td>Oxide ceramic substance, particularly Zirconium oxide containing sub- stance, and stabilizer, particularly rare earth oxides, preferably Yttrium oxide or Cerium oxide</td>
<td>100 to 2000μm, preferably 150 to 500μm</td>
</tr>
<tr>
<td>Smoothing Layer</td>
<td>Oxide ceramic substance, particularly Zirconium oxide containing sub- stance, and stabilizer, particularly rare earth oxides, preferably Yttrium oxide or Cerium oxide</td>
<td>1 to 50μm, preferably 10 to 30μm</td>
</tr>
</tbody>
</table>

**Brief Description of the Drawings**

In the following, embodiments of the invention will be further described, with reference to the accompanying drawings, in which:

Fig. 1 shows a schematic sectional view of a heat shield layer system manufactured according to the embodiment of the invention described herein after; and
Fig. 2 shows a microscopic picture of a heat shield layer system manufactured according to that embodiment, in which the different layer structures are evident.

**EXAMPLE 1**

In the present embodiment for manufacturing a heat shield layer system by means of the LPPS coating process according to the invention, first, a barrier layer is applied under thin film conditions. Thereafter, a primer layer and a hot gas corrosion protection layer is deposited under thick film conditions. Then, a coat of a protection layer is applied under thin film conditions; and finally, a smoothing layer is applied under thin film conditions.

The resultant heat shield coating system comprises a structure as seen in Fig. 1. The reference numerals have the following meaning:

1. The substrate (e.g. Ni- or Co-Alloy);
2. Metallic barrier layer (e.g. NiAl- or NiCr-Alloy - 1 to 20 µm);
3. Metallic hot gas corrosion protection layer (e.g. MCrAlY-Alloy - 50 to 500 µm);
4. Oxide ceramic protection layer (e.g. Al₂O₃ - 1 to 20 µm);
5 Oxide ceramic heat shield layer (e.g. ZrO$_2$-8%Y$_2$O$_3$ - 100 to 2000 μm);
6 Oxide ceramic smoothing layer (e.g. ZrO$_2$-8%Y$_2$O$_3$ - 1 to 50 μm).

It is understood that the above described embodiment is not to be considered as limiting at all, but that other layer systems different than the one described herein above can be applied, of course within the scope of the appended claims. Particularly, the present invention provides for applying the individual layers in every arbitrary sequence.

EXAMPLE 2

Following the process described in Example 1 herein above, the layer sequence illustrated in Fig. 2 has been manufactured. The parameters are as follows:

10 Substrate Superalloy Inconel® 718, 3mm thick
11 Barrier Layer AMDRY® (Ni80%Cr), 13μm thick
12 Hot Gas Corrosion Protection Layer AMDRY® 9951 (Co 32%Ni 21%CR 8%Al 0.5%Y), 137μm thick
13 Protection Layer Metco 105 (99.5% Al$_2$O$_3$) 9μm thick
14 Heat Shield Layer Metco 204, ZrO$_2$-8%Y$_2$O$_3$, 360μm thick
15 Smoothing Layer Metco 204, ZrO$_2$-8%Y$_2$O$_3$, 15μm thick.

* Trademarks
WHAT IS CLAIMED IS:

1. A process for applying a heat shielding coating system on a metallic substrate, said coating system comprising, starting from said metallic substrate, the following individual layers in the following sequence:
   a metallic barrier layer consisting of a metal alloy and having a thickness of 1 to 20 μm;
   a hot gas corrosion protection layer having a thickness of 50 to 500 μm and consisting of a MCrAlY-alloy, M being a member of the group consisting of Fe, Co, and Ni, or of a metal aluminide;
   an oxide ceramic protection layer for the protection of said hot gas corrosion protection layer having a thickness of 1 to 20 μm;
   an oxide ceramic heat barrier layer having a thickness of 100 to 2000 μm; and
   an oxide ceramic smoothing layer having a thickness of 1 to 50 μm;
   wherein each layer of said entire coating system being applied to said metallic substrate by low pressure plasma spraying in a single operation cycle without changing the coating technology or equipment.

2. The process according to claim 1 in which said coating system is heat treated as a whole after having been applied to said substrate.

3. The process according to claim 1 in which said barrier layer serving as diffusion barrier or metallic donator has a thickness of 8 to 12 μm.

4. The process according to claim 1 in which said metal alloy of the barrier layer is a NiAl- or a NiCr-alloy.
5. The process according to claim 1 in which said metallic hot gas corrosion protection layer has a thickness of 100 to 300 μm.

6. The process according to claim 1 wherein said oxide ceramic protection layer has a thickness of 8 to 12 μm.

7. The process according to claim 1 in which said oxide ceramic protection layer consists of an aluminum oxide or a ternary Al-Zr-O-compound.

8. The process according to claim 1 in which said oxide ceramic heat barrier layer has a thickness of 150 to 500 μm.

9. The process according to claim 1 in which said oxide ceramic heat barrier layer consists of an oxide ceramic substance and a stabilizer.

10. The process according to claim 9 wherein said oxide ceramic substance is a zirconium oxide containing substance.

11. The process according to claim 10 wherein said stabilizer is made of a rare earth oxide.

12. The process according to claim 11 wherein said rare earth oxide is yttrium oxide or cerium oxide.

13. The process according to claim 1 in which said oxide ceramic smoothing layer has a thickness of 10 to 30 μm.

14. The process according to claim 13 in which said oxide ceramic smoothing layer consists of an oxide ceramic substance and a stabilizer.
15. The process according to claim 14 wherein said oxide ceramic substance is zirconium oxide containing substances.

16. The process according to claim 15 wherein said stabilizer is made of a rare earth oxide.

17. The process according to claim 16 wherein said rare earth oxide is yttrium oxide or cerium oxide.

18. The process according to claim 1 in which said metallic substrate is moved by simple rotating in a particle cloud of a plasma jet associated with said low pressure plasma spraying.

19. The process according to claim 1 in which the application of said coating system is performed by low pressure plasma spraying according to a thin film method for said metallic barrier layer, said oxide ceramic heat barrier layer and said smooth oxide ceramic surface layer.

20. The process according to claim 1 in which said metallic substrate is a turbine blade.

21. The process according to claim 20 wherein said turbine blade is a stator blade or a rotor blade of a stationary gas turbine or an aircraft jet engine.

22. The process according to claim 21 in which said metallic substrate is a component of a stationary gas turbine or of an aircraft jet engine that is subjected to hot gas.

23. The process according to claim 22 wherein said component is a heat shield.
24. Metallic component made of a Ni- or Co-alloy, having a heat shielding coating system comprising, starting from said metallic component, the following individual layers in the following sequence:

   a metallic barrier layer consisting of a metal alloy and having a thickness of 1 to 20 \( \mu \)m;

   a hot gas corrosion protection layer having a thickness of 50 to 500 \( \mu \)m and consisting of a MCrAlY-alloy, \( M \) being a member of the group consisting of Fe, Co, and Ni, or of a metal aluminide;

   an oxide ceramic protection layer for the protection of said hot gas corrosion protection layer having a thickness of 1 to 20 \( \mu \)m;

   an oxide ceramic heat barrier layer having a thickness of 100 to 2000 \( \mu \)m; and

   an oxide ceramic smoothing layer having a thickness of 1 to 50 \( \mu \)m;

   wherein each layer of said entire coating system is applied to said metallic component by low pressure plasma spraying in a single operation cycle without changing the coating technology or equipment.