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(54) **Process for obtaining protective coatings for high temperature with high roughness and coating obtained**

(57) The invention describes a process which allows obtaining a protective coating against oxidation at high temperature comprising a layer of MCrAlY material wherein M is selected from the group consisting of Ni, Co, Fe and their mixtures, characterised by a high surface roughness in its outer part, and high density, cohesion and reduced oxidation in its inner part. The process comprises the thermal projection of MCrAlY-based powders by high frequency pulsed detonation techniques, at different projection distances, to form the compact and dense inner part and the rough outer part. The coatings obtained can be heat treated in an inert atmosphere and can be used as bonding for a thermal barrier layer.

EP 2 202 328 A1

Description

Field of the Invention

[0001] The present invention is comprised within the field of protective coatings against the corrosion-oxidation of metal components subjected to high temperatures such as for example the blades of a gas turbine. The invention particularly relates to a process which allows obtaining a new improved coating.

Background of the Invention

[0002] MCrAly-based coatings, wherein M is a metal selected from Ni, Co and Fe, are normally used for protecting metal components which are subjected to high temperatures, such as for example the blades of a gas turbine.

[0003] The object of these coatings is to protect said metal components or substrates against the corrosion and oxidation occurring at high temperature, for which reason a layer formed by a ceramic heat insulator or thermal barrier is occasionally applied thereon. In this case, MCrAly-based coatings must work as protective barriers against corrosion and oxidation, and additionally as intermediate adaptation or bond layers for fixing the layer formed by a ceramic heat insulator or thermal barrier.

[0004] These coatings are obtained by deposition by means of the different thermal projection techniques and especially by means of vacuum plasma spray (VPS) techniques, air plasma spray (APS) techniques, high velocity oxygen fuel (HVOF) thermal projection techniques or detonation processes.

[0005] The quality and usefulness of these MCrAlY coatings for a given composition is directly related to their density and internal cohesion and generally to a microstructure preventing the presence of cracks allowing the corrosive attack on the substrate. On the other hand, it is important for them to have a certain surface roughness affecting the degree of adherence of the ceramic layers or thermal barriers deposited thereon.

[0006] However, obtaining dense bond layers, for their functionality as a protective barrier against corrosion and oxidation at high temperatures, and at the same time with high roughness, is very difficult for traditional projection techniques, VPS and HVOF, which must use materials in the form of poweder with a fine grain size (<65 microns) to achieve the desired degree of density and internal cohesion. On the other hand, the high energy density of the flame produced by these processes makes it necessary to project at distances that are relatively far from the substrate for the purpose of limiting the thermal impact on the substrate. In these circumstances, the roughness results obtained are insufficient and less than 10 microns Ra.

[0007] As a solution to the previous problems US2008/0145643, US2005/0260434 and US5817372 disclose processes in which a "double" bond layer is deposited in the sense that it is formed by a dense first sublayer obtained according to the indicated processes, and by a second MCrAlY sub-layer thereon, in which the density has been sacrificed in favour of a high roughness. In these processes two different types of powders and specific projection conditions for each one are used, which obviously introduces an additional complication into the process, both in terms of reproducibility and technical quality and in a higher cost for the overall processing.

[0008] Application US2007/1190900 describes a process in which an attempt is made to generate a rough surface in the deposited MCrAlY layer by means of a post-treatment by means of ionic bombardment, whereby regardless of the technical difficulty, equipment difficulty or costs which it involves, only limited improvements in the surface roughness have been achieved, always less than 10 microns Ra.

[0009] It is known that the use of air plasma spray (APS) techniques is common for the mentioned application of this type of coating, which techniques allow forming an MCrAlY layer with high roughness, as a result of using powder with a large grain size. However, said MCrAlY layers have a lower effectiveness from the point of view of protecting the substrate against the corrosive attack, as a result of their high porosity or absence of compactness. This takes places because of the comparatively reduced impact speed of the particle projected by means of APS, resulting in layers with lower density and therefore a more limited anti-corrosive protective behaviour.

[0010] Another alternative of the state of the art to achieve said features is obtaining coatings from MCrAly powders with a size larger than the normal one (> 65 microns) by using high frequency pulsed detonation (HFPD) techniques. A coating with higher roughness is thereby generated although this entails a greater internal porosity, such that said approach must be used only in the upper layers of the MCrAly coating as part of a layer with a double structure, result of the use of two different types of powders. The added complexity that said approximation involves due to the use of specific and different powders to form the rough MCrAlY layer is evident.

[0011] Therefore and in view of that set forth it is still necessary in the state of the art to provide a new process which allows obtaining alternative MCrAlY type coatings having good roughness and density properties.

Description of the Drawings

[0012]

Figure 1 is a metallographic micrograph of the microstructure corresponding to the section of an MCrAlY layer of a coating obtained according to the process of the invention. The inner area (1) with high density and the surface area (2) with high roughness are seen.

Figure 2 is a metallographic micrograph of the microstructure corresponding to the section of an MCrAlY layer of a coating obtained according to the process of the invention. The inner area (1) with high density and the surface area (2) with high roughness are seen.

Description of the Invention

[0013] In one aspect the invention relates to a new process which can be carried out continuously and simply, using a single type of powder, to obtain a protective coating for protecting against oxidation at high temperature on a substrate. The process, hereinafter the process of the invention, comprises a step pf thermal projection of MCrAlY powder to obtain an MCrAlY layer on said substrate by means of a high frequency pulsed detonation (HFPD) technique, in which at least two different projection distances are used. According to the process of the invention M is selected from the group consisting of Ni, Co, Fe and their mixtures.

[0014] The protective coating obtained by means of the process of the invention forms an additional aspect of the present invention which is also described in detail. This coating comprises an MCrAlY layer with high density and low oxidation. This layer has in turn an outer part having a high surface roughness equal to or greater than 10 microns Ra, and is **characterised in that** its microstructure (porosity and internal cohesion) differs between the inner part of the layer and the outer part of the layer.

[0015] In the context of the present invention the part which is in direct contact with the substrate on which the protective coating is deposited is referred to as the inner part of the MCrAlY layer and the opposite part of the MCrAlY layer which is optionally in contact with a second layer of the coating is referred to as the outer part. This second layer is hereinafter also referred to as thermal barrier layer.

[0016] The process of the invention is carried out using high frequency pulse detonation (HFPD) projection techniques which are conventional and are described for example in WO97/23299, WO97/23301, WO97/23302, WO97/23303, WO98/29191, WO99/12653, WO99/37406 and WO01/30506. These techniques use the gas flows produced during the cyclic explosions or detonations to accelerate and project the coating material and differ from the detonation techniques known as D-gun, in the absence of mechanical valves or other mobile elements, a pulsed behaviour being achieved from the actual dynamic of the fluids, from a continuous gas supply. Electronically controllable high frequency explosions are thus achieved which can exceed 100 Hz compared to the frequencies of a D-gun process working between 1 and 10 Hz. The generation of high or low temperature explosions is carried out using combustion gases such as propane, propylene, methane or natural gas, with oxygen, and controlling the mixture of gases involved in each explosion. These techniques allow depositing materials such as those used in the present invention, achieving a good adherence and compaction as a result of the detonation process. Furthermore, it is possible to achieve a greater productivity since the frequency of the explosions can be controlled.

[0017] In the process of the present invention and during the step of thermal projection by means of (HFPD), the material to be deposited is introduced into the barrel in the form of powder, accompanied by a carrier gas through a supply port. Said powder merges with the mixture of explosive gases in said barrel and as a consequence of the explosive process, it is entrained, heated and accelerated by the generated gaseous flow until impacting on the substrate to be coated, giving rise to the formation of the MCrAlY layer by means of a thermal projection process. Given the cyclical nature of the detonation projection technique, the mentioned process occurs cyclically to each explosion.

[0018] The deposition of MCrAlY powders by means of HFPD can easily be controlled and optimised by a person skilled in the art to achieve a high density, a good compaction and adherence of the coating with minimal internal oxidation, thus requiring a low temperature of the detonation process and a low oxygen environment during the projection.

[0019] Detonation frequencies greater than 60 Hz are generally used to improve the productivity of the process and reduce the volume of gases used in each explosion. The MCrAlY powders are introduced into the barrel of the detonation gun at a point close to its outlet, at a distance from the detonation chamber between 100 and 500 mm.

[0020] As has been previously defined, the process of the invention comprises the use of at least two different projection distances.

[0021] In this sense, in a particular embodiment of the process of the invention at least one first projection distance greater than 100 mm is used to form the inner part of the MCrAlY layer of the protective coating in direct contact with the substrate, and another subsequent distance lower than 100 mm is used to form the outer part of the MCrAlY layer.

[0022] For distances greater than 100 mm, the process of the invention is carried out using the known parameters which are described in patent application W02006/042872 which can be optimised to obtain a layer with high density, cohesion and reduced oxidation. For distances lower than 100 mm the parameters can be the same or be varied.

[0023] Obviously between one and the other, the projection distances can be varied forming as many subparts of the MCrAlY layer as projection distances are used in the process of the invention.

[0024] In this sense, according to a particular embodiment of the process of the invention, such process is carried out using (i) a first projection distance greater than 100 mm, (ii) a last projection distance less than 100 mm and (iii) at least one intermediate projection distance between the first and the last distance. During the process of the invention the use of these projection distances can be made according to single continuous sequence without needing interruptions, such that the change of distance can be made during the projection without needing to turn off the gun.

[0025] The inventors of the present invention have observed that in the process of the invention the use of projection distances lower than 100 mm generate a greater degree of porosity and lower internal cohesion in the deposited layer. This is due to the inclusion within the layer of non-molten particles which are larger in size or are deposited at a lower impact speed (peripheral area of the projection beam) but which nevertheless have enough energy to remain adhered during the cyclic deposition process. On the other hand when the projection distances are greater than 100 mm the mentioned non-molten particles do not form part of the coating, given that the actual explosive process generates cyclic gas flows eliminating the possible weakly adhered non-molten particles from the surface which may have been deposited in previous cycles. The result is a layer with higher density and internal cohesion, formed only by the deposited particles with higher kinetic energy which have withstood the gas flow of each explosion.

[0026] The MCrAlY layer is generally used as a bond layer for a thermal barrier layer in which case the presence of an especially rough surface (indicatively Ra > 10 microns) which improves the adherence and mechanical compatibility between both layers is of interest.

[0027] For these cases, and according to a particular embodiment of the process of the invention, the projection distance is modified during the last deposition cycles of the step of thermal projection, typically by means of the suitable robot handling programme, to obtain the MCrAlY layer which is especially rough and suitable to act as a bond layer for ceramic thermal barrier layers.

[0028] The cyclic nature of the detonation process allows the heat flow applied on the substrate-layer during the deposition to be less than that used in alternative techniques such as plasma projection or HVOF, enabling the projection at very short distances (<100 mm) without local overheating.

[0029] The process of the invention optionally further comprises carrying out a step of heat treatment of the MCrAlY layer in an inert atmosphere, for example a N2 atmosphere. This treatment promotes the diffusion process leading to a microstructure of the MCrAlY layer more suitable for protecting against corrosion-oxidation under extreme conditions.

[0030] The process can further comprise a step of thermal projection or deposition of a layer of a heat insulating material on the MCrAlY layer. This step of thermal projection or deposition of the thermal barrier layer is carried out by means of a suitable conventional technique, which can be selected from vacuum plasma spray (VPS), air plasma spray (APS), physical vapour deposition (PVD), high velocity oxygen fuel (HVOF) thermal projection, detonation and high frequency pulsed detonation (HFPD).

[0031] The heat insulating material, forming said thermal barrier, is formed by a ceramic normally belonging to the zirconia family such as Zr02-Y203, ZrO2-MgO, ZrO2-CaO among others.

[0032] One of the most important advantages of the process of the invention in view of what has been set forth lies in the fact that it uses a single type of powder. Said powder is, in a particular embodiment, a CoNiCrAlY type alloy for example. The use of a single type of powder allows the process of the new invention to be optionally carried out in a single operation. In this sense, the deposition of the mentioned MCrAly coating is optionally carried out according to a single and continuous sequence, without there being interruptions linked to changes of powder or of equipment. The resulting process is simpler, faster, cheaper and allows obtaining a coating comprising a MCrAlY layer with high density, internal cohesion and reduced oxidation in the inner part thereof and simultaneously a surface in the outer part characterised by a high roughness.

[0033] As has been mentioned previously, the protective coating obtained according to the process of the present invention forms an additional aspect of the present invention.

[0034] Said coating comprises an MCrAlY layer the thickness of which can vary within wide margins. Said thickness is generally comprised between 50 and 200 microns. The relative thickness of each of the parts can also vary and depends in each case, among other factors, on the conditions of the process for obtaining it, such as for example on the projection time during which each of the at least two different projection distances is used.

[0035] The coating of the invention comprises an MCrAlY layer which is characterised by having a high roughness (indicatively greater than or equal to 10 microns Ra) in its outer part.

[0036] In a particular embodiment the coating of the invention comprises, in addition to the MCrAlY layer with said roughness, a thermal barrier layer thereon. Said thermal barriers have a porous nature and can be deposited using any conventional thermal projection or deposition technique as has already been mentioned above.

[0037] Illustrative examples of the invention are described below which are set forth for a better understanding of the invention and in no case must they be considered a limitation of the scope thereof.

Examples

Example 1:

[0038] CoNiCrAlY powders (Praxair Ni-535-4) were used.

[0039] The projection was carried out by means of the high frequency pulsed detonation HFPD technique with the following parameters:

- Natural gas flow (slpm): 60

- Propylene flow (slpm): 60
- Oxygen flow (slpm): 190
- Frequency (Hz): 70
- Nitrogen carrier gas (slpm): 55

[0040] In these conditions, the detonation barrel was handled in an automated manner at an initial distance of 150 mm to generate the dense microstructure of the inside (1) and subsequently at a distance of 70 mm to give rise to the rough surface (2).

- Projection distance (mm): variable 150 and 70

[0041] With these parameters a CoNiCrAlY coating was achieved comprising a compact structure with one layer, the outer part of which has a surface roughness (microns) of Ra 11 and Rz 55.7 (depth of roughness).

[0042] The microstructure resulting from the metallographic preparation of a section of said coating is shown in Figure 1.

Example 2:

[0043] CoNiCrAlY (Sulzer 4700) powders were used. The projection was carried out by means of the high frequency detonation technique with the following parameters:

- Natural gas flow (slpm): 60
- Propylene flow (slpm): 60
- Oxygen flow(slpm): 190
- Frequency (Hz): 80
- Nitrogen carrier gas (slpm): 55

[0044] In these conditions, the detonation barrel was handled in an automated manner at an initial distance of 150 mm to generate the dense microstructure of the inside (1) and subsequently at a distance of 70 mm to give rise to the rough surface (2).

- Projection distance (mm): variable 150 and 50

[0045] With these parameters a CoNiCrAlY coating was achieved comprising a compact structure with one layer, the outer part of which has a surface roughness (microns) of Ra 13.9 and Rz 74.2 .

[0046] The microstructure resulting from the metallographic preparation of a section of said coating is shown in Figure 2.

Claims

1. Process for obtaining a protective coating against oxidation at high temperature on a substrate comprising a step of thermal projection of MCrAlY powder, wherein M is selected from the group consisting of Ni, Co, Fe and their mixtures, to obtain an MCrAlY layer on said substrate by means of a high frequency pulsed detonation technique, wherein at least two different projection distances are used.

2. Process according to claim 1, wherein a first projection distance greater than 100 mm is used to form the inner part of the MCrAlY layer of the protective coating in direct contact with the substrate and another subsequent distance less than 100 mm is used to form the outer part of the MCrAlY layer.

3. Process according to claim 1 or 2, wherein: (i) a first projection distance greater than 100 mm, (ii) a last projection distance less than 100 mm and (iii) at least one intermediate projection distance between the first and the last distance is used.

4. Process according to any one of claims 1 to 3, wherein the use of the projection distances is made according to a single continuous sequence without interruptions.

5. Process according to any one of claims 1 to 4, wherein a single type of powder is used.

6. Process according to claim 5, wherein the powder used is of the CoNiCrAlY type.

7. Process according to any one of claims 1 to 6, further comprising a step of heat treatment, in an inert atmosphere, of the MCrAlY layer.

8. Process for obtaining a protective coating according to any one of claims 1 to 7, further comprising a step of thermal projection or deposition of a layer of a heat insulating material on the MCrAlY layer.

9. Process according to claim 8, wherein the thermal projection or deposition of the thermal barrier layer is carried out by means of a suitable technique, selected from vacuum plasma spray (VPS), air plasma spray (APS) technique, physical vapour deposition (PVD), high velocity oxygen fuel (HVOF) thermal projection, detonation and high frequency pulsed detonation (HFPD).

10. Process according to claim 8 or 9, wherein the heat insulating material is selected from ZrO_2-based ceramic materials.

11. Protective coating obtainable according to the process defined in any one of claims 1 to 10.

12. Protective coating having an MCrAlY layer wherein M is selected from Ni, Co, Fe and their mixtures, having an outer part and an inner part, the outer part having a surface roughness equal to or greater than 10 microns Ra, and said layer being **characterised**

in that its microstructure differs between the inner part of the layer and the outer part of the layer.

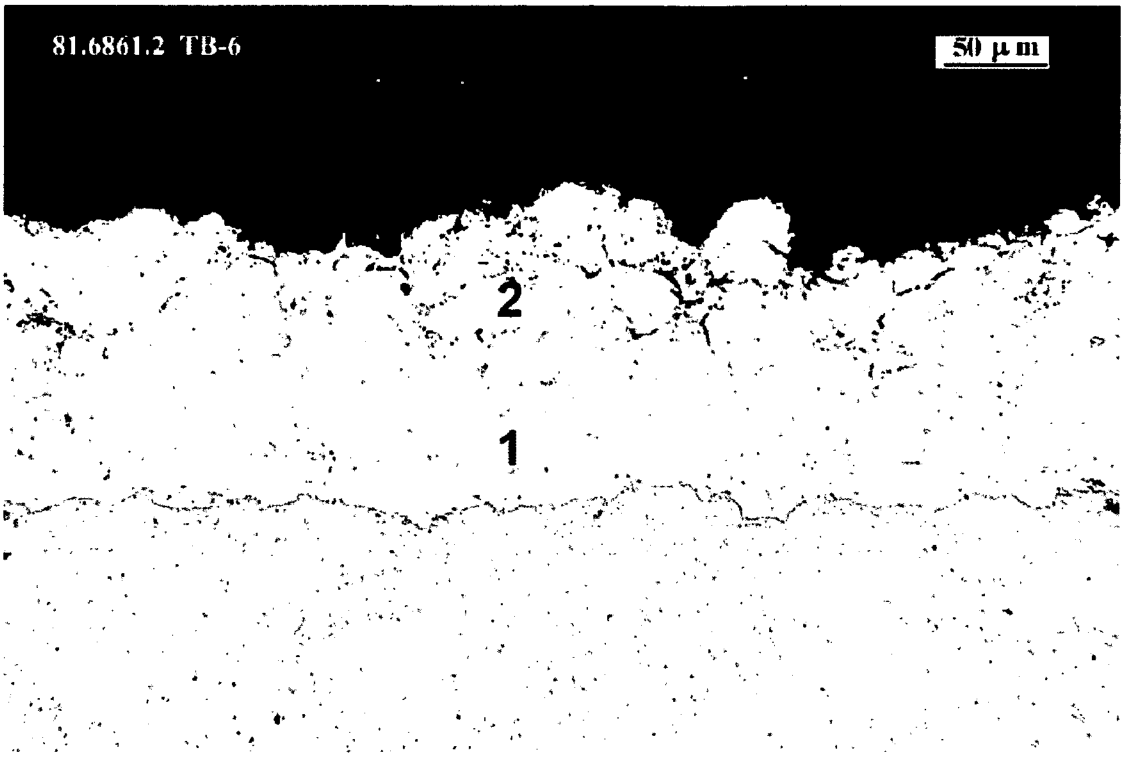

FIG. 1

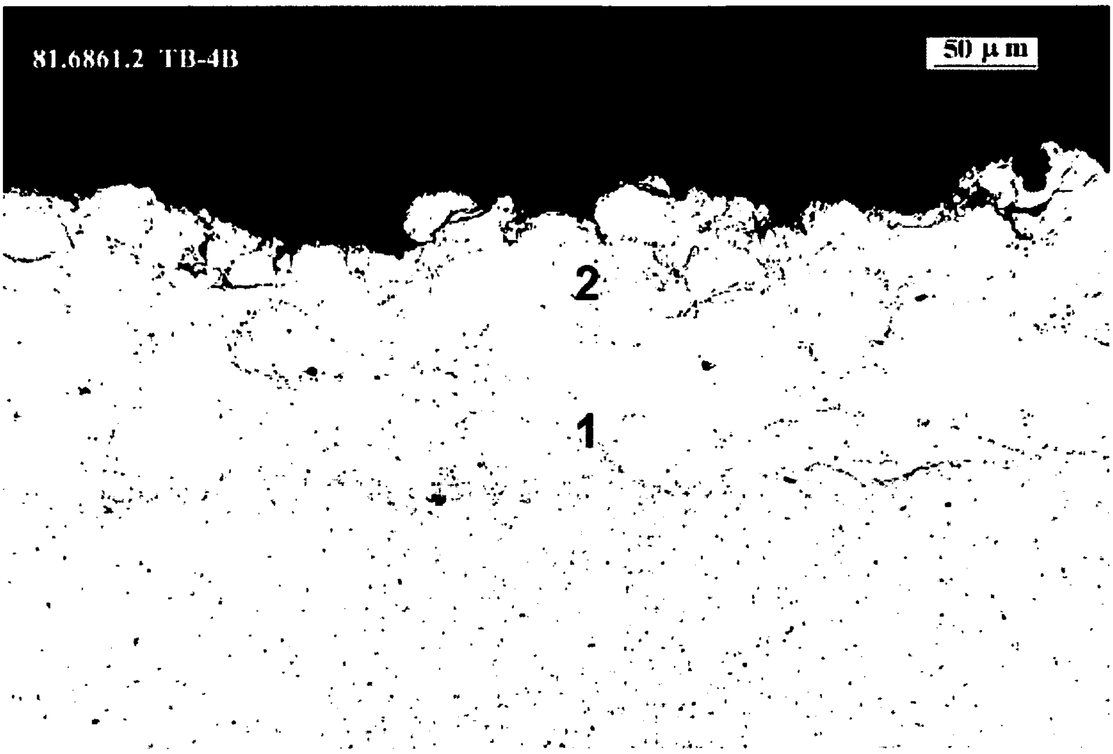

FIG. 2

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EUROPEAN SEARCH REPORT

Application Number
EP 08 38 0344

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	18 May 2009	Chalaftris, Georgios

CATEGORY OF CITED DOCUMENTS

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