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(54) **Method for applying a high-temperature stable coating layer on the surface of a component and component with such a coating layer**

(57) The invention proposes a method for applying a high-temperature stable coating layer (12) on the surface of a component (11), comprising the steps of:

- a) providing a component (11) with a surface to be coated;
b) providing a powder material containing at least a fraction of submicron powder particles (18);

- c) applying said powder material to the surface of the component (11) by means of a spraying technique to build up a coating layer (12), whereby
d) said sub-micron powder particles (18) are each at least partially surrounded by an oxide shell (20) and establish with their oxide shells (20) an at least partially interconnected sub-micron oxide network (22) within said coating layer (12).

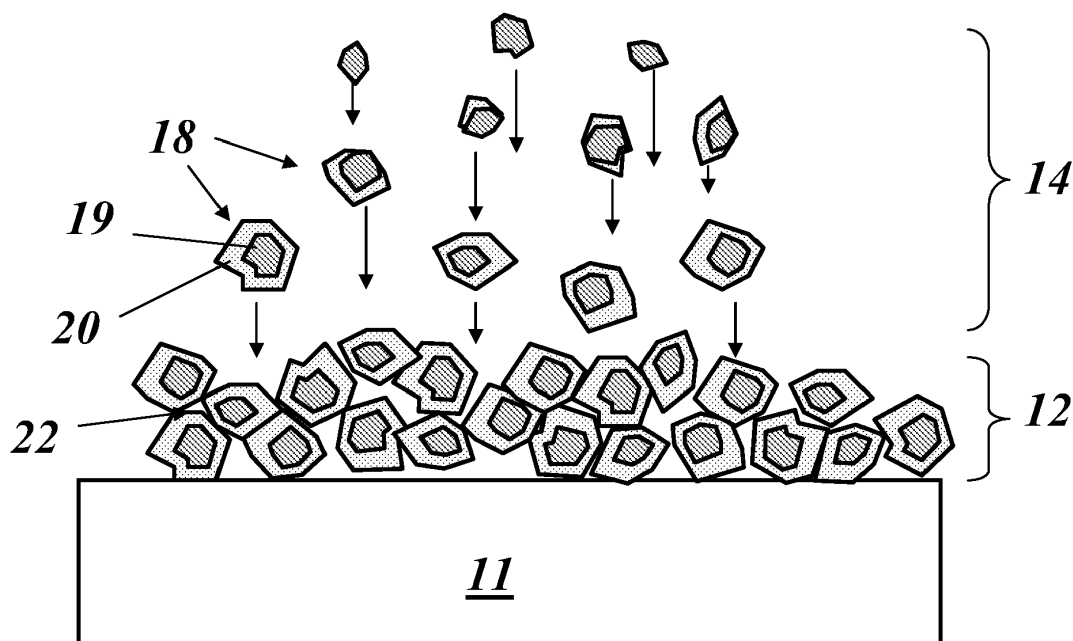


Fig.2

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to thermally loaded components of thermal machines, especially gas turbines. It refers to a method for applying a high-temperature stable coating layer on the surface of a component. It further refers to a component with such a coating layer.

PRIOR ART

[0002] In order to protect thermally loaded components against hot gases they are coated with various protective layers, for example a thermal barrier coating (TBC). To bond such a layer firmly to the body of the component, a bond coat may be provided between the base material of the component and the TBC. A well-known bond coat material for a component made of a Ni base superalloy or the like, is of the type MCrAlY, where M stand for a metal, e.g. Ni.

[0003] During service life, cracks might form in the bond coat and propagate into the base metal of components, which are part of gas turbine or other thermal machine, and which are exposed to high operating temperatures. Especially, low cycle fatigue (LCF)/thermo-mechanical fatigue (TMF) cracking is a limiting factor for the lifetime and the reconditionability of such components.

[0004] In the current situation, lifetime and reconditionability limits for the state of the art design and engine operation mode are specified based on calculation and experience. No solution is currently commercially available with the standard MCrAlY composition of the bond coat/overlay coat in order to extend these limits (both oxidation life and mechanical life at the same time). A self healing system would be a solution to extend them.

[0005] A different approach using nano-structured coating is presented in document US 7,361,386 B2.

[0006] According to this document, in order to increase the efficiency of gas turbine engines, the hot-section stationary components (mainly combustors, transition pieces, and vanes) are protected with thermal barrier coatings (TBCs). In addition to providing the thermal insulation to the nickel-based superalloy components, TBCs also provide protection against high temperature oxidation and hot corrosion attack. The conventional TBCs that are used in naval (diesel) engines, in military and commercial aircraft, and in land-based gas turbine engine components, consist of a duplex structure made up of a metallic MCrAlY (M stands for either Co, Ni and/or Fe) bond coat and Ytria partially stabilized zirconia (YPSZ) ceramic top coat.

[0007] The document further asserts that the full potential of the YPSZ TBCs is yet to be realized due mainly to the cracking problem that occurs along or near the bond coat/top coat interface after a limited number of cycles of engine operation. This interfacial cracking, often leading to premature coating failure by debonding (spal-

lation) of the top coat from the bond coat, has been amply demonstrated from microstructural evidence that was obtained from in-service degradation of deposited coatings as well as from laboratory experiments that have been conducted. The thin oxide layer that grows on top of the bond coat, at the bond coat/top coat interface, plays a critical role in the interface cracking. It is quite evident that this cracking problem negatively impacts the coating performance by reducing both the engine efficiency (because the engine operating temperature is kept below its optimum temperature) and the lifetime of the engine components. In turn, this greatly affects the reliability and the efficiency of the entire engine system.

[0008] According to document US 7,361,386 B2, the bond coat surface, onto which the YPSZ top coat is disposed, has a thin oxide layer that consists mostly of various oxides (NiO, Ni(Cr,Al)₂O₄, Cr₂O₃, Y₂O₃, Al₂O₃). The presence of this thin oxide layer plays an important role in the adhesion (bonding) between the metallic bond coat and the ceramic top coat. However, during engine operation, another oxide layer forms in addition to the native oxide. This second layer, also mostly alumina, is commonly referred to as the thermally grown oxide (TGO) and slowly grows during exposure to elevated temperatures. Interfacial oxides, in particular the TGO layer, play a pivotal role in the cracking process. It is believed that the growth of the TGO layer leads to the build up of stresses at the interface region between the TGO layer and top coat.

[0009] To solve these problems, document US 7,361,386 B2 proposes to modify the microstructure of the MCrAlY bond coat (in a thermal barrier coating) in a controlled way prior to exposure to high temperatures, in order to control the subsequent changes during high temperature exposure. More specifically, the structure, composition, and growth rate of the thermally grown oxide (TGO) is controlled to ultimately improve the performance of TBCs. According to US 7,361,386 B2, a nanostructure is provided in the bond coat and, consequently, nanocrystalline dispersoids are introduced into the structure. The purpose of the dispersoids is to stabilize the nanocrystalline structure and to nucleate the desirable [alpha]-Al₂O₃ in the TGO.

[0010] Other prior art documents, Ajdelsztajn et al. in Surf. & Coat. Tech. 201 (2007) 9462-9467 and Funk et al. in Met. Mat. Trans. A 42 [8] (2011) 2233-2241, show that such a nano-structured bond coat has several advantages like for e.g. improved mechanical properties. Such benefit is due to the presence of ultrafine dispersoids of γ and β phases.

SUMMARY OF THE INVENTION

[0011] It is an object of the present invention to provide a method for applying an improved high-temperature stable coating layer on the surface of a component and a component being used in a high-temperature environment, which is coated with such coating layer.

[0012] This object is obtained by a method according to claim 1 and a component according to claim 14.

[0013] The method according to the invention for applying a high-temperature stable coating layer on the surface of a component, comprises the steps of:

- a) providing a component with a surface to be coated;
- b) providing a powder material containing at least a fraction of sub-micron powder particles;
- c) applying said powder material to the surface of the component by means of a spraying technique to build up a coating layer, whereby
- d) said sub-micron powder particles are each at least partially surrounded by an oxide shell and establish with their oxide shells an at least partially interconnected sub-micron oxide network within said coating layer.

[0014] According to an embodiment of the inventive method said powder material is applied to the surface of the component by means of a thermal spraying technique.

[0015] Especially, the thermal spraying technique used is one of High Velocity Oxygen Fuel Spraying (HVOF), Low Pressure Plasma Spraying (LPPS), Air Plasma Spraying (APS) or Suspension Plasma Spraying (SPS).

[0016] According to another embodiment of the inventive method said powder material has the form of agglomerates.

[0017] According to a further embodiment of the inventive method said powder material has the form of a suspension.

[0018] According to another embodiment of the inventive method the powder material contains powder particles of micron size and/or larger agglomerates, and that the sub-micron powder particles are in said coating layer distributed around the surface of said powder particles of micron size and/or said larger agglomerates.

[0019] According to just another embodiment of the inventive method the sub-micron powder particles are pre-oxidized before being incorporated into said coating layer.

[0020] Preferably, the pre-oxidation takes place in-flight during spraying.

[0021] Alternatively, the pre-oxidation is done by an oxidative pre heat treatment of the powder material.

[0022] According to another embodiment of the inventive method the powder material is a metallic powder.

[0023] Especially, the powder material is of the MCrAlY type with M = Ni, Co, Fe or combinations thereof.

[0024] According to just another embodiment of the inventive method the coating layer is a bond coat or an overlay coating.

[0025] According to the invention, said component having a surface, which is coated with a coating layer is characterized in that said coating layer comprises sub-micron powder particles, which are each at least partially

surrounded by an oxide shell and establish with their oxide shells an at least partially interconnected sub-micron oxide network within said coating layer.

[0026] According to an embodiment of the invention, said coating layer further comprises powder particles of micron size and/or larger agglomerates.

[0027] Especially, said sub-micron powder particles are in said coating layer distributed around the surface of said powder particles of micron size and/or said larger agglomerates.

[0028] According to another embodiment of the invention the coating layer is a bond coat and the powder material is of the MCrAlY type with M = Ni, Co, Fe or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The present invention is now to be explained more closely by means of different embodiments and with reference to the attached drawings.

Fig. 1 shows in a simplified schematic diagram a thermal spray configuration, which can be used for the present invention;

Fig. 2 shows the creation of a coating layer with an internal oxide network by in-flight oxidation of sprayed sub-micron powder particles according to an embodiment of the invention;

Fig. 3 shows - similar to Fig. 2 - the embedding of micron particles or agglomerates in said sub-micron powder particle oxide network; and

Fig. 4 shows schematically a graded coating layer in accordance with an embodiment of the invention.

DETAILED DESCRIPTION OF DIFFERENT EMBODIMENTS OF THE INVENTION

[0030] The present invention discloses a specific type of sub-micron structured coating. Due to a sub-micron scale oxide network and fine grain microstructure, the invention aims to reduce the LCF/TMF cracking.

[0031] Another aspect of the invention is the retardant effect for the oxidation and the corrosion. Due to the nano-scale oxide network of the bond coat/overlay coating, the impact by oxidation and corrosion is slowed down.

[0032] In consequence, the invention should enable a longer service life and/or assure reconditionability with less scrap parts and/or decreased operation risks, such as crack formation in critical area of the component due to mechanical/thermal load, and/or oxidation/corrosion and/or FOD (Foreign Objects Damage) events.

[0033] The invention enables:

- the preservation of a sub-micron structure during ap-

plication of the coating by thermal spraying techniques and during turbomachine operation (at least for an extended operation period compared to the state-of-the art nano-structured coatings);

- additional improvements of coating properties.

[0034] The novelty of the invention is the use of a sub-micron powder (at least to a certain percentage of the total powder mixture) and the way to process it (preparation and thermal spray application) to reach the mentioned improved coating properties. The improved coating behavior is particularly based on a reduced TMF/LCF effect of the coating with (at least partial) sub-micron structure.

[0035] The invention is based on:

(1) The use of powder with sub-micron size or a powder containing at least a portion of such sub-micron powder:

- either in form of agglomerates, consisting of at least a portion of such sub-micron powder, processed by thermal spray techniques like HVOF, LPPS or APS, for example (see Fig. 1);
- or in form of a suspension including at least a portion of such sub-micron powder, when applied by thermal spray techniques like suspension plasma spray (SPS).

[0036] Such powder is a metallic powder, preferably a MCrAlY with M= Ni, Co, Fe or combinations thereof.

[0037] In-flight oxidation during spraying (see Fig. 2) has the effect of pre-oxidizing the sub-micron powder of the agglomerate or suspension. Pre-oxidation can also be achieved by oxidative pre heat treatment of the powder mixture. When only a portion of the powder exhibits a sub-micron scale, it is preferable to have the sub-micron particles distributed around the surface of the micron and/or agglomerated spray powder particles.

(2) The application of the powder on a component of a turbo machine by thermal spray methods (HVOF, LPPS, APS, SPS etc.) in order to form a (at least partially) sub-micron structured coating with (at least a partially) oxide network. Air gun spray technologies can also be used. The use of pre-oxidized spray powder is preferred. A homogeneous or a graded coating can be applied (see the graded coating layer 12b in Fig. 4). For example, the graded layer 12b can have an oxide content, which increases or decreases with the distance from the surface of the base metal to the top surface of the coating. In a different example the oxide content could have a minimum in the middle of the coating thickness.

(3) The function of such a coating can be as bond coat, overlay coating or a thermal barrier coating system for turbo machine components like gas turbine

blades or vanes. The coating of the invention can be used alone or in combination with other standard coatings. The coating of the invention can be used on newly made components or reconditioned components and can also locally be applied for the partial (surface) repair of components.

(4) The component with such a coating, benefits during operation from:

- Oxidation protection:

Due to the presence of an oxide shell (20) around the particles, the losses of reactive elements (for example Y, Al and C) during the thermal spray process are reduced. In consequence, a more stable thermally grown oxide (TGO) can be formed during service by diffusion mechanism, slowing down the oxidation mechanism during operation compared to conventional metallic coating systems. In parallel, the oxide network (22) formed by the connecting oxide shells (20) allows to reduce the build-up of the depletion zone in the coating (top and interface to the base metal) by slowing down the diffusion mechanism.

- Corrosion protection:

With the current invention, Chromium is finely dispersed in the coating. This enables a faster gathering of sulfur and a slowing down of the corresponding corrosion process(es).

- Mechanical lifetime:

The mechanical lifetime is improved compared to conventional coating systems, due to several effects:

1) The improved coating oxidation properties enable to reduce the overall coating thickness. As a consequence, the risk of crack formation due to TMF and LCF is also reduced. This effect implies the slowing down of formation and propagation of respective damages, such as cracks.

2) Due to the 3D-oxide network (22), the mechanical load is more homogeneously distributed along the oxide network, which reduces the risks of sudden failure.

3) The depletion zone in the coating is reduced due to less interdiffusion with the base metal and the atmosphere

(environment). In consequence, the risk of brittle phase precipitation (potential sites for crack initiation) in the base metal/coating is reduced.

4) The oxide shell slows down the grain coarsening in the coating microstructure and with this another root cause for crack formation.

5) When the oxide-network is disrupted due to cracking, the metallic core of sub-micron particles can diffuse into the metallic coating matrix. By subsequent local oxidation, potential cracks can be filled up.

6) The metallic matrix ductility is increased due to the fine grain structure, which is also beneficial for the overall coating lifetime.

[0038] Fig. 1 shows a typical thermal spray configuration 10, which can be used to apply the sub-micron powder coating layer according to the invention. The thermal spray configuration 10 comprises a spray gun 13, which is supplied with the sub-micron powder 15, a fuel 16 and an oxidant 17. By burning the fuel 16, a flame 14 is generated, which transports the powder particles to the surface of a component 11, thereby building the coating layer 12.

[0039] During the transport in the flame 14 the sub-micron powder particles 18 undergo a reaction, as can be seen in Fig. 2, such that they are transformed into particles having a (metallic) core 19 surrounded by an oxide shell 20. Within the coating layer 12, those oxidized sub-micron particles build up an interconnected structure with a sub-micron oxide network 22.

[0040] When the powder material is a mixture of sub-micron particles 18 and micron powder particles or agglomerates 21, as shown in Fig. 3, the resulting coating layer 12a comprises those agglomerates or micron powder particles 21 being surrounded by oxidized sub-micron powder particles 18.

[0041] One additional embodiment of the invention is a manufacturing process for an improved thermal barrier coating system of highly thermally and especially cyclically liner segment of a gas turbine by

- a) providing an homogeneous metallic powder material made of NiCrAlY type with Ni = balancing element, Cr = 25 wt%, Al=5 wt%, Y=0.7 wt%, containing 30 wt% of pre-oxidised sub-micron powder particles agglomerated with microsized powder particles (20-50 micron) of same chemical composition,
- b) said sub-micron powder particles (<1 micron) are each surrounded by an oxide shell (50-100 nm) and establish with their oxide shells an at least partially interconnected 3D sub-micron oxide network in the final coating layer application,
- c) applying said powder material to the surface of

the vane by means of High Velocity Oxygen Fuel (HVOF) spraying technique to build up a homogeneous bondcoating layer with a thickness of 250 micron, and

d) the bondcoat layer is subsequently over coated with a ceramic thermal barrier coating (300-600 micron).

[0042] The result is a bondcoat / thermal barrier coating system with improved TMF and oxidation resistance with the capability of forming stable TGO scales, leading to an improved overall coating lifetime.

[0043] A further embodiment of the invention is a manufacturing process for a graded metallic overlay coating system of highly thermally and especially cyclically loaded turbine vane of a gas turbine by

- a) providing a first homogeneous metallic powder material and a second homogeneous metallic powder material, each of them have a chemical composition of NiCrAlY type with Ni = balancing element, Cr = 26 wt%, Al=6 wt%, Y=0.8 wt%,
- b) wherein the first powder blend contains 25 wt% of pre-oxidised submicron (<1 micron; 50-100 nm oxide shell) powder particles agglomerated (average 80 micron) with microsized powder particles (20-50 micron) of same chemical composition,
- c) and wherein the second powder containing micro-size powder particles (20-50 micron),
- d) applying the first powder material to the surface of the liner segment by means of High Velocity Oxygen Fuel (HVOF) spraying technique to build up a homogeneous first coating layer with a thickness 80 micron,
- e) applying the second powder material to the surface of the first coating layer by means of High Velocity Oxygen Fuel (HVOF) spraying technique (250 micron),
- f) applying another layer of first powder material on top of the second layer by means of High Velocity Oxygen Fuel (HVOF) spraying technique (80 micron),
- g) the first and third layer contains each at least a partially interconnected 3D submicron oxide network.

[0044] The result is a graded metallic overlay coating system with improved TMF and oxidation resistance, leading to an improved overall coating lifetime.

[0045] In general, the initiation and propagation of damages within coatings exhibiting an at least partial sub-micron scale structure is retarded compared to conventional coating microstructures. The "sub-micron effect" is retained over extended lifetime periods, also due to the (at least partial) oxide network. Such aspects of the invention give to the coating a so-called self healing characteristic.

[0046] Therefore the following advantage are reached

with the invention: Longer service life and/or reduced amount of scrap parts during reconditioning and/or reduced operation risks and/or cost reduction related to crack restoration, oxidation and corrosion damage. In addition, the fine grain sized coating allows a diffusion heat treatment with a reduced number of heat treatment cycles. A nano coating as top layer improves the TMF and oxidation resistance, which results in an improved overall coating lifetime.

LIST OF REFERENCE NUMERALS

[0047]

10	thermal spray configuration
11	component
12, 12a, 12b	coating layer (e.g. bond coat)
13	spray gun
14	flame
15	powder
16	fuel (e.g. gaseous)
17	oxidant
18	sub-micron powder particle
19	metallic core
20	oxide shell
21	agglomerated or micron powder particle
22	oxide network (sub-micron)

Claims

1. Method for applying a high-temperature stable coating layer (12, 12a, 12b) on the surface of a component (11), comprising the steps of:
 - a) providing a component (11) with a surface to be coated;
 - b) providing a powder material containing at least a fraction of submicron powder particles (18);
 - c) applying said powder material to the surface of the component (11) by means of a spraying technique to build up a coating layer (12, 12a, 12b), whereby
 - d) said sub-micron powder particles (18) are each at least partially surrounded by an oxide shell (20) and establish with their oxide shells (20) an at least partially interconnected sub-micron oxide network (22) within said coating layer (12, 12a, 12b).
2. Method according to claim 1, **characterized in that** said powder material is applied to the surface of the component (11) by means of a thermal spraying technique.
3. Method according to claim 2, **characterized in that** the thermal spraying technique used is one of High

Velocity Oxygen Fuel Spraying (HVOF), Low Pressure Plasma Spraying (LPPS), Air Plasma Spraying (APS) or Suspension Plasma Spraying (SPS).

4. Method according to one of the claims 1-3, **characterized in that** said powder material has the form of agglomerates.
5. Method according to one of the claims 1-3, **characterized in that** said powder material has the form of a suspension.
6. Method according to one of the claims 1-5, **characterized in that** the powder material contains powder particles (21) of micron size and/or larger agglomerates, and that the sub-micron particles powder particles (18) are in said coating layer (12, 12a, 12b) distributed around the surface of said powder particles (21) of micron size and/or said larger agglomerates.
7. Method according to one of the claims 1-6, **characterized in that** the submicron powder particles (18) are pre-oxidized before being incorporated into said coating layer (12, 12a, 12b).
8. Method according to claim 7, **characterized in that** the pre-oxidation takes place in-flight during spraying.
9. Method according to claim 7, **characterized in that** the pre-oxidation is done by an oxidative pre heat treatment of the powder material.
10. Method according to one of the claims 1-9, **characterized in that** the powder material is a metallic powder.
11. Method according to claim 10, **characterized in that** the powder material is of the MCrAlY type with M = Fe, Ni, Co or combinations thereof.
12. Method according to one of the claims 1-11, **characterized in that** the coating layer (12, 12a, 12b) is a bond coat or an overlay coating.
13. Component (11) for being used in a high-temperature environment, said component (11) having a surface, which is coated with a coating layer (12, 12a, 12b), **characterized in that** said coating layer (12, 12a, 12b) comprises sub-micron powder particles (18), which are each at least partially surrounded by an oxide shell (20) and establish with their oxide shells (20) an at least partially interconnected sub-micron oxide network (22) within said coating layer (12, 12a, 12b).
14. Component according to claim 13, **characterized in**

that said coating layer (12, 12a, 12b) further comprises powder particles (21) of micron size and/or larger agglomerates.

15. Component according to claim 14, **characterized in that** said sub-micron powder particles (18) are in said coating layer (12, 12a, 12b) distributed around the surface of said powder particles (21) of micron size and/or said larger agglomerates.
16. Component according to one of the claims 13-15, **characterized in that** the coating layer (12, 12a, 12b) is a bond coat and the powder material is of the MCrAlY type with M = Ni, Co, Fe or combinations thereof.

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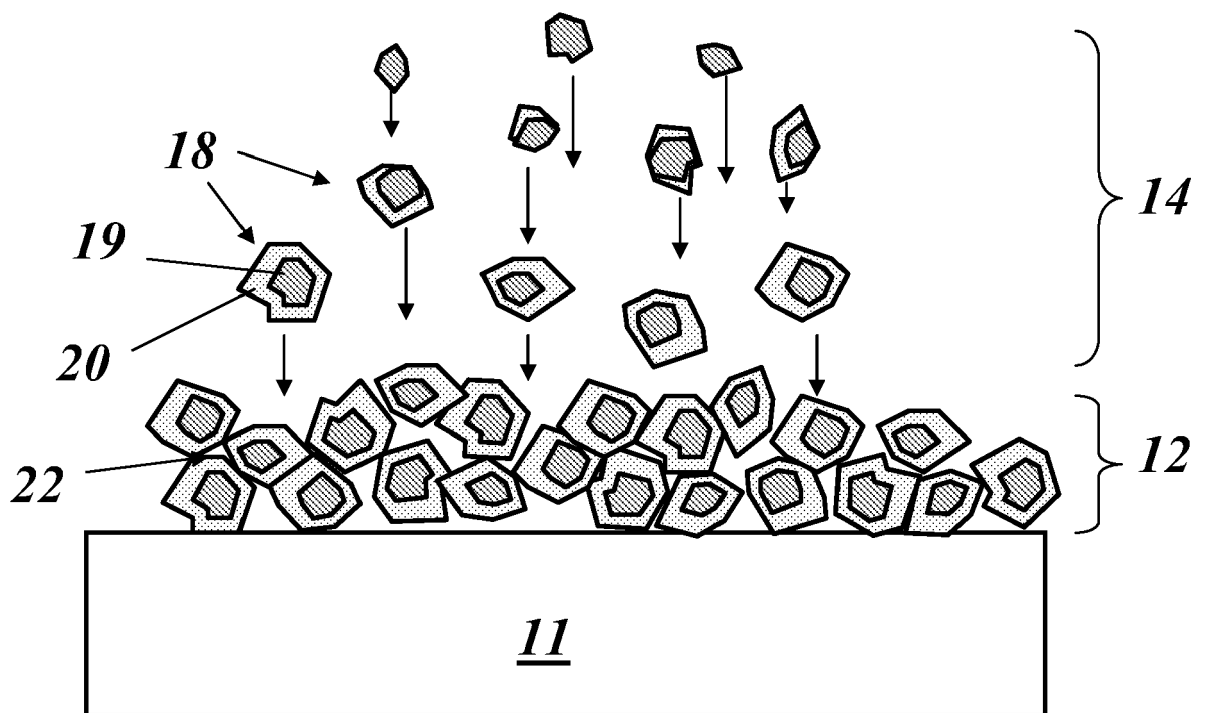
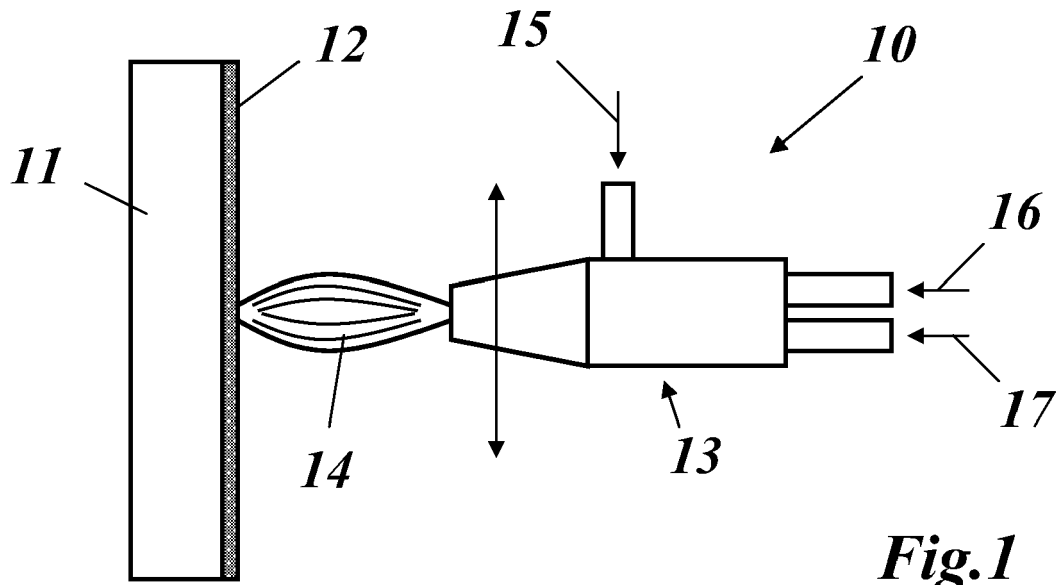
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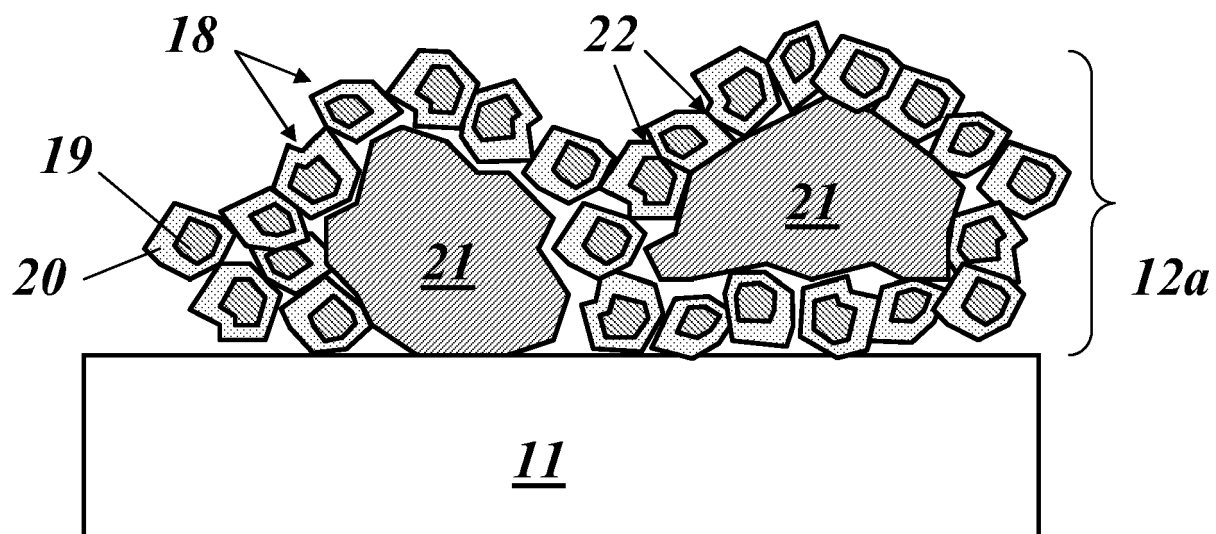


Fig. 3

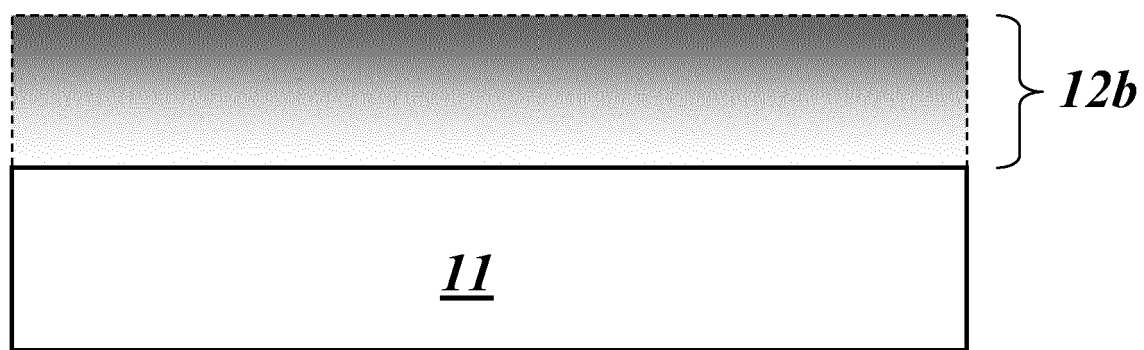


Fig. 4



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**ANNEX TO THE EUROPEAN SEARCH REPORT
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