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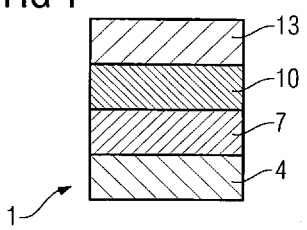
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(54) Title: LAYERED COATING SYSTEM WITH A MCRALX LAYER AND A CHROMIUM RICH LAYER AND A METHOD TO PRODUCE IT

FIG 1



(57) Abstract: The invention relates to a layer system with a MCrX layer and a Cr-rich layer on the MCrX layer.

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LAYERED COATING SYSTEM WITH A MCRALX LAYER AND A CHROMIUM RICH LAYER AND A METHOD TO PRODUCE IT

The invention relates to a layered system with a MCrAlX layer, a Cr-rich layer that is uniquely resistant to both oxidation and hot corrosion and a method to produce such a system. Preferably an aluminide layer is applied.

EP0587341 describes a high temperature corrosion resistant composite coating where the process includes the following steps:

- Applying an alloy coating material of the MCrAlY type.
- Optionally chromizing the MCrAlY type coating to produce a coating with a chromized top layer having extra chromium in solid solution in the M constituent of the coating.
- Aluminising the coating to produce a coating having a surface layer containing aluminides of the M constituent of the coating.
- Depositing a platinum layer on top of the surface of the aluminised coating.

EP 1327702 describes a MCrAlY coating system comprising an inner layer of beta-NiAl and an outer layer of gamma/beta-MCrAlY and TBC. In the document it is stated that the oxidation resistance can be improved for theses layers of coating by adding 0.1-4% Si. The coatings are deposited using a gas phase method, CVD, PVD etc..

US 2005/0003227 describes a similar system as in US ' 227, but here is also an intermediate layer of a platinum type of metal included. In the document it is stated that the oxidation resistance can be improved for these layers of coating by adding 0.1-4% Si.

EP 1029100/US 6416882 describes a MCrAlY type of bond coat comprising up to 2% silicon.

Aluminide and/or chromium modified coating systems are also described in US 7,229,701, US 6,183,888, US 7,060,366, US 6,287,644, EP 1 082 216, US 6,001,492, US 5,507,623, EP 1 541 808 and US 6,569,492.

EP 0587341 describes a high temperature corrosion resistant composite coating where the process includes the following steps:

- Applying an alloy coating material of the MCrAlY type.
- Optionally chromizing the MCrAlY type coating to produce a coating with a chromized top layer having extra chromium in solid solution in the M constituent of the coating.
- Aluminising the coating to produce a coating having a surface layer containing aluminides of the M constituent of the coating.
- Depositing a platinum layer on top of the surface of the aluminised coating.

But these coatings are still not good enough.

It is therefore the aim of the invention to solve this problem.

The problem is solved by a layer system according to claim 1 and a method to produce it according to claim 27.

In the dependent claims further advantageous embodiments are listed which can be combined arbitrarily to get further advantages.

The concept behind the invention is based on different coating chemistries being suited to protect a substrate within certain temperature and environmental criteria. For example during high temperature oxidation an outer ß-NiAl-layer provides the protection by forming a tenacious thin Alumina oxide in reaction with the high temperature and oxygen in the system, this reaction is typical of the similar ß-NiAl coatings found in industry and well documented in literature. At temperatures of around 750°C to 800°C up to around 950°C a broad front attack can occur depleting unprotected substrate materials of Cr and Al. Again the use of an Alumina forming ß-NiAl coating will protect against type I corrosion. However, for type II corrosion, localized pitting type corrosion is more likely. Molten salts in the gas stream combined with SO_2 and SO_3 condense onto the turbine components resulting in small pits in the surface. The best defense for such attack is the introduction of a Cr rich coating system. The important aspect of the invention is that the Cr rich layer is continuous and is as thermally stable as possible, therefore if the components are operating in a type II corrosion environment the ß-NiAl is consumed, however, the corrosion damage is restricted to the outer layer of ß-NiAl and the continuous α-Cr layer provides suitable protection, additions of elements which add to the coatings corrosion protection such as, but not limited to Si or Hf. A strain complaint base layer is added in the form of an MCrAlY coating, which provides a degree of strain compliance as well as a final layer of protection should the ß-NiAl and α-Cr be compromised. By design then, the layered coating structure essentially allows the environment to "select" the coating composition most suitable to provide protection. The concept can be clearly demonstrated in figure 3. The introduction of Si or other beneficial elements can increase the expected life of the α-Cr layer.

It shows

Figure 1 to 5 examples of a layer system
Figure 6 a gas turbine
Figure 7 a blade
Figure 8 a combustion chamber.
The figures and the description are only embodiments of the invention.
Figure 1 shows one exemplary component 1 as a layer system of the invention.

The component 1 has a metallic substrate 4 which preferably comprises a heat resistant cast or wrought nickel or cobalt alloy, which is preferably Hastelloy X.

Preferably on the substrate 4 in (a.) in Fig. 4) an inner or lowest MCrX layer 7 is applied, especially only one MCrX layer 7 is applied in (b.) in Fig. 4) where X is yttrium (Y) and/or silicon (Si) and/or boron (B) and/or aluminum (Al).
The inner MCrX layer 7 comprises MCrAlX' with X' at least Yttrium (Y) and is preferably only Yttrium (Y).
This inner MCrAlX' layer 7 comprises especially a NiCrAlY layer and very especially comprises in at% Ni, 22% Cr, 10% Al, 1,0% Y, especially consists of Amdry 962.
The inner MCrX layer 7 is preferably applied by HVOF.
The inner MCrX layer 7 is also preferably direct on the substrate 4.

On or in this inner MCrX layer 7 a chromium rich layer 10 is applied on (c.) in Fig. 4)), especially an α-Cr-layer.
The chromizing is preferably performed from 1000°C to 1150°C preferably from 1 to 6 hours, very preferably at 1050°C -1075°C for 2h to 4h.
The chromizing treatment will lead at least partly to a diffusion layer on the inner layer 7 (Therefore the reference 7 in Fig 4 c) represents the thickness of the

inner layer 7 or that a diffusion layer is present and not one composition). The chromium rich layer 10 is preferably a diffusion layer.

This layer system 1 is preferably heat treated, so that the overlay Cr layer is diffused into the inner MCrAlX' layer 7.

Preferably on this α-chromium layer 10 an additional further nickel based layer, a first outer MCrX'' layer 13 is applied on which is preferably the outer most layer (d.) in Fig. 4). This MCrX'' layer X'' is preferably silicon (Si) and boron (B).
Furthermore, the first outer MCrX'' layer 13 can be a silicon and/or boron-containing nickel chromium alloy Ni-Cr-Si-B.
This first outer MCrX'' layer 13 has a different composition than the inner layer 7 and is very especially a NiCrSiB layer (Amdry 103 which consists of in at% 74% Ni, 17% Cr, 9.2% Y, 9%Si, 0.1% B).

After applying the MCrX'' (NiCrSiB) layer, preferably performed by HVOF, a stabilizing heat treatment is preferably performed. This stabilizing heat treatment is performed at temperatures preferably 1000°C to 1200°C preferably for 1 to 6 hours, preferably at 1000 to 1025°C for 6h.

Preferably a second outer layer 19 is present on or in the first outer layer 13. The second outer layer 19 is an aluminum rich layer as shown in figure 3.
Preferably the outer layer 19 is a diffusion layer.

The first outer MCrX'' layer 13 can be aluminized to achieve the second outer layer 19 (e.) in Fig. 4).
The aluminizing treatment is performed at temperatures preferably from 1050°C to 1115°C preferably for1 to 10

hours, preferably at 1070°C to 1095°C for 7h. Preferably there is a final anneal treatment preferably at 1000°C to 1150°C for 1 to 6 hours, preferably at 1080°C for 2h, very preferably in vacuum.

In figure 2 a further embodiment of the invention is shown.
The component 1 has a metallic substrate 4 which preferably comprises a heat resistant cast or wrought nickel or cobalt alloy.
In figure 2 this substrate is preferably "Hastelloy X™" a commercially available wrought nickel alloy that nominally contains 47% Ni, 22 Cr, 18.5 Fe, 9 Mo, 1.5 Co, 1 Si, 1 Mn, 0.1 C.

Preferably on the substrate 4 (a.) in Fig. 5) first inner MCrX layer 7 is applied (b.) in Fig. 5), especially only two MCrX' layer 7', 16 are applied, where
X' is at least yttrium (Y) and is preferably only Yttrium (Y).
This first inner MCrAlX' layer 7' comprises especially a NiCrAlY layer and very especially comprises in at% 67% Ni, 22% Cr, 10% Al, 1,0% Y, especially consists of Amdry 962.
The first inner MCrAlX' layer 7' is preferably applied by HVOF.

A second inner layer 16 is applied on the first inner MCrAlX' layer 7' (c.) in Fig. 5). The layer 16 is especially a MCrX'' layer with X'' = Si and/or B.
This additional layer 16 has a different composition than the first inner layer 7' and is very especially a NiCrSiB layer (Amdry 103 which consists of in at% 74 Ni, 17 Cr, 9.2 Si, 0.1 B).
The second inner layer 16 is preferably applied by HVOF.

On or in this second inner layer 16 a chromium rich layer 10 is applied on, especially an α-Cr-layer (d.) in Fig. 5, therefore the reference 16 in Fig 5 d) represents the thickness of the inner layer 16 or that a diffusion layer is present and not one composition).
The chromizing is preferably performed from 1000°C to 1150°C preferably for 1 to 6 hours, preferably at 1050°C - 1075°C for 2h to 4h.

The chromizing treatment will preferably lead to diffusion layer on the first inner layer 7'.
This layer system 1 is preferably heat treated, so that the overlay α-Cr is diffused into the inner MCrAlX' layer 7'.

On the chromium rich layer 10 an aluminide layer 22 is applied (e.) in Fig. 5).
This is preferably achieved by Ni-plating the chromium rich layer 10 and aluminizing this plated Ni-Layer. The Ni-plate has preferably has a thickness of 10µm to 20µm.
Preferably an annealing heat treatment after Ni-plating is performed, preferably at 1121°C for preferably 2h.
This annealing treatment is preferably performed in vacuum.

The following aluminizing is performed preferably at 1080°C for preferably 7h.
After aluminizing a final annealing heat treatment is performed, preferably at 1080°C for 2h.
This annealing treatment is preferably performed in vacuum.

A general remark: The chromizing or aluminizing can lead to diffusion layers as shown in Figures 4, 5 or as overlays as shown in Figures 1, 2 or 3. But this is not limiting. Both features can be present.

Another preferred example is described in the following:

Base coat:	MCrAlY sprayed by HVOF or Plasma (could be sprayed by suitable alternative such as VPS or LPPS).
Cr Rich Layer:	Applied by CVD or above-the-source Chromizing methods. It was found that a 4 h Chromizing cycle was required to ensure a stable Cr layer during subsequent annealing processes.
Ni:	Ni plating 10μm to 20μm
Aluminizing:	Applied by CVD or above the source Aluminizing methods. Final annealing would be required to reintroduce the mechanical properties of the substrate materials.

Another proposal is to apply a coating system using the following configuration where Si has been introduced in the coating:

Base Coat:	MCrAlY sprayed by HVOF or Plasma (could be sprayed by suitable alternative such as VPS or LPPS).
Cr Rich Layer:	The MCrAlY was over chromized by CVD or above-the-source methods for 4hours. This was followed by application of NiCrSiB (Amdry 103 powder or similar chemistry powder) using HVOF or Plasma methods (could be sprayed by suitable alternative such as VPS or LPPS).
Aluminizing:	Applied by CVD or above the source Aluminizing methods.

Final annealing would be required to reintroduce the mechanical properties of the substrate materials.

Figure 6 shows, by way of example, a gas turbine 100 in the form of a longitudinal part section. In its interior, the gas turbine 100 has a rotor 103, which is mounted such that it can rotate about an axis of rotation 102 and has a shaft 101, also known as the turbine rotor. An intake housing 104, a compressor 105 a, for example toroidal, combustion chamber 110, in particular an annular combustion chamber, with a plurality of coaxially arranged burners 107, a turbine 108 and the exhaust casing 109 follow one another along the rotor 103. The annular combustion chamber 110 is in communication with a, for example annular, hot-gas duct 111 where, for example, four successive turbine stages 112 form the turbine 108.

Each turbine stage 112 is formed, for example, from two blade or vane rings. As seen in the direction of flow of a working medium 113, a row 125 formed from rotor blades 120 follows a row 115 of guide vanes in the hot-gas duct 111.

The guide vanes 130 are secured to an inner housing 138 of a stator 143, whereas the rotor blades 120 of a row 125 are fitted to the rotor 103, for example by means of a turbine disk 133. A generator or machine (not shown) is coupled to the rotor 103.

When the gas turbine 100 is operating, the compressor 105 sucks in air 135 through the intake housing 104 and compresses it. The compressed air which is provided at the turbine-side end of the compressor 105 is passed to the burners 107, where it is mixed with a fuel. The mixture is then burnt in the combustion chamber 110 to form the

working medium 133. From there, the working medium 133 flows along the hot-gas duct 111 past the guide vanes 130 and the rotor blades 120. The working medium 113 expands at the rotor blades 120, transferring its momentum, so that the rotor blades 120 drive the rotor 103 and the rotor drives the machine coupled to it.

When the gas turbine 100 is operating, the components which are exposed to the hot working medium 113 are subject to thermal loads. The guide vanes 130 and rotor blades 120 of the first turbine stage 112, as seen in the direction of flow of the working medium 113, together with the heat shield elements which line the annular combustion chamber 110, are subject to the highest thermal loads. To withstand the temperatures prevailing there, these components can be cooled by means of a coolant.

It is likewise possible for substrates of the components to have a directional structure, i.e. they are in single-crystal form (SX structure) or include only longitudinally directed grains (DS structure). By way of example, iron-base, nickel-base or cobalt-base superalloys are used as material for the components, in particular for the turbine blades and vanes 120, 130 and components of the combustion chamber 110. Superalloys of this type are known, for example, from EP 1 204 776 B1, EP 1 306 454, EP 1 319 729 A1, WO 99/67435 or WO 00/44949; these documents form part of the present disclosure with regard to the chemical composition of the alloys.

The blades and vanes 120, 130 may likewise have coatings to protect against corrosion (MCrAlX; M is at least one element selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), X is an active element and stands for yttrium (Y) and/or silicon and/or at least one of the rare earth elements or hafnium). Alloys of this type are known from EP 0 486 489 B1, EP 0 786 017 B1, EP 0

412 397 B1 or EP 1 306 454 A1, which are intended to form part of the present disclosure with regard to the chemical composition.

A thermal barrier coating consisting, for example, of ZrO_2, Y_2O_4-ZrO_2, i.e. it is not, is partially or is completely stabilized by yttrium oxide and/or calcium oxide and/or magnesium oxide, may also be present on the MCrAlX. Columnar grains are produced in the thermal barrier coating by suitable coating processes, such as for example electron beam physical vapor deposition (EB-PVD).

The guide vane 130 has a guide vane root (not shown here) facing the inner housing 138 of the turbine 108 and a guide vane head on the opposite side from the guide vane root. The guide vane head faces the rotor 103 and is fixed to a securing ring 140 of the stator 143.

Figure 7 shows a perspective view of a rotor blade 120 or guide vane 130 of a turbo machine, which extends along a longitudinal axis 121.

The turbo machine may be a gas turbine of an aircraft or of a power plant for generating electricity, a steam turbine or a compressor.

The blade or vane 120, 130 has a securing region 400, an adjoining blade or vane platform 403 and a main blade or main part 406 in succession along the longitudinal axis 121. As guide vane 130, the vane 130 may have a further platform (not shown) at its vane tip 415.

A blade or vane root 183, which is used to secure the rotor blades 120, 130 to a shaft or disk (not shown), is formed in the securing region 400. The blade or vane root 183 is designed, for example, in hammerhead form. Other

configurations, such as fir-tree or dovetail root, are also possible. The blade or vane 120, 130 has a leading edge 409 and a trailing edge 412 for a medium which flows past the main blade or vane part 406.

In the case of conventional blades or vanes 120, 130, by way of example, solid metallic materials, in particular superalloys, are used in all regions 400, 403, 406 of the blade or vane 120, 130. Superalloys of this type are known, for example, from EP 1 204 776 B1, EP 1 306 454, EP 1 319 729 A1, WO 99/67435 or WO 00/44949; these documents form part of the present disclosure with regard to the chemical composition of the alloy. The blade or vane 120, 130 may in this case be produced by a casting process, also by means of directional solidification, by a forging process, by a milling process or combinations thereof.

Work pieces with a single-crystal structure or structures are used as components for machines which are exposed to high mechanical, thermal and/or chemical loads during operation. Single-crystal work pieces of this type are produced, for example, by directional solidification from the melt. This involves casting processes in which the liquid metallic alloy is solidified to form the single-crystal structure, i.e. the single-crystal work piece, i.e. directionally. In the process, dendritic crystals are formed in the direction of the heat flux and form either a columnar-crystalline grain structure (i.e. with grains which run over the entire length of the work piece and are referred to in this context, in accordance with the standard terminology, as directionally solidified) or a single-crystal structure, i.e. the entire work piece consists of a single crystal. In this process, the transition to globular (polycrystalline) solidification needs to be avoided, since non-directional growth inevitably leads to the formation of transverse and longitudinal grain boundaries, which negate the good

properties of the directionally solidified or single-crystal component. Where directionally solidified microstructures are referred to in general, this is to be understood as encompassing both single crystals, which do not have any grain boundaries or at most have small-angle grain boundaries, and columnar crystal structures, which do have grain boundaries running in the longitudinal direction, but do not have any transverse grain boundaries. In the case of these latter crystalline structures, it is also possible to refer to directionally solidified microstructures (directionally solidified structures). Processes of this type are known from US 6,024,792 and EP 0 892 090 A1; these documents form part of the present disclosure.

The blades or vanes 120, 130 may also have coatings protecting against corrosion or oxidation, e.g. (MCrAlX; M is at least one element selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), X is an active element and stands for yttrium (Y) and/or silicon and/or at least one rare earth element, or hafnium (Hf)). Alloys of this type are known from EP 0 486 489 B1, EP 0 786 017 B1, EP 0 412 397 B1 or EP 1 306 454 A1, which are intended to form part of the present disclosure with regard to the chemical composition of the alloy.

It is also possible for a thermal barrier coating consisting, for example, of ZrO_2, Y_2O_4-ZrO_2, i.e. which is not, is partially or is completely stabilized by yttrium oxide and/or calcium oxide and/or magnesium oxide, to be present on the MCrAlX. Columnar grains are produced in the thermal barrier coating by suitable coating processes, such as for example electron beam physical vapor deposition (EB-PVD).

The term refurbishment means that protective layers may have to be removed from components 120, 130 after they

have been used (for example by sandblasting). Then, the corrosion and/or oxidation layers or products are removed. If necessary, cracks in the component 120, 130 are also repaired using the solder according to the invention. This is followed by recoating of the component 120, 130, after which the component 120, 130 can be used again.

The blade or vane 120, 130 may be of solid or hollow design. If the blade or vane 120, 130 is to be cooled, it is hollow and may also include film cooling holes 418 (indicated by dashed lines).

Figure 8 shows a combustion chamber 110 of a gas turbine 100 (Fig. 6).

The combustion chamber 110 is configured, for example, as what is known as an annular combustion chamber, in which a multiplicity of burners 107, which are arranged around an axis of rotation 102 in the circumferential direction, open out into a common combustion chamber space 154, with the burners 107 producing flames 156. For this purpose, the combustion chamber 110 overall is of annular configuration, positioned around the axis of rotation 102.

To achieve a relatively high efficiency, the combustion chamber 110 is designed for a relatively high temperature of the working medium M of approximately 1000°C to 1600°C. To allow a relatively long operating time even with these operating parameters, which are unfavorable for the materials, the combustion chamber wall 153 is provided with an inner lining formed from heat shield elements 155 on its side facing the working medium M. Each heat shield element 155 made from an alloy is equipped on the working medium side with a particularly heat-resistant protective layer (MCrAlX layer and/or ceramic coating) or is made from material that is able to withstand high temperatures

(solid ceramic bricks). These protective layers may be similar to the turbine blades or vanes, i.e. meaning for example MCrAlX: M is at least one element selected from the group consisting of iron (Fe), cobalt (Co), nickel (Ni), X is an active element and stands for yttrium (Y) and/or silicon and/or at least one rare earth element, or hafnium (Hf). Alloys of this type are known from EP 0 486 489 B1, EP 0 786 017 B1, EP 0 412 397 B1 or EP 1 306 454 A1, which are intended to form part of the present disclosure with regard to the chemical composition of the alloy.

It is also possible for a, for example, ceramic thermal barrier coating to be present on the MCrAlX, consisting, for example, of ZrO_2, Y_2O_4-ZrO_2, i.e. it is not, is partially or is completely stabilized by yttrium oxide and/or calcium oxide and/or magnesium oxide.

Columnar grains are produced in the thermal barrier coating by suitable coating processes, such as for example electron beam physical vapor deposition (EP-PVD).

The term refurbishment means that protective layers may have to be removed from heat shield elements 155 after they have been used (for example by sandblasting). Then, the corrosion and/or oxidation layers or products are removed. If necessary, cracks in the heat shield element 155 are also repaired using the solder according to the invention. This is followed by recoating of the heat shield elements 155, after which the heat shield elements 155 can be used again.

Moreover, on account of the high temperatures in the interior of the combustion chamber 110, it is possible for a cooling system to be provided for the heat shield elements 155 and/or for their holding elements. The heat shield elements 155 are in this case, for example, hollow

and may also include film cooling holes (not shown) which open out into the combustion chamber space 154.

Patent claims

1. Layer system (1)
comprising
a substrate (4)
at least one MCrX layer (7, 7', 16) on the substrate (4),
especially one MCrX layer (7, 7') as lowest layer (7, 7'),
especially direct on the substrate (4),
wherein X is at least yttrium (Y) and/or silicon (Si) and/or aluminum (Al) and/or boron (B),
wherein M is nickel (Ni) and/or cobalt (Co) and
a chromium-rich layer (10) on or in the at least one MCrX layer (7, 16).

2. Layer system according to claim 1,
wherein only one lowest MCrX layer (7) is present on the substrate (4) and
under the chromium-rich layer (10).

3. Layer system according to claim 1,
wherein only two MCrX layers (7', 16) are present on the substrate (4) and
under the chromium-rich layer (10).

4. Layer system according to claim 2,
wherein the lowest MCrX layer (7) is a MCrAlX' layer,
wherein X' is at least Yttrium (Y),
especially X' is Y.

5. Layer system according to claim 3,
wherein the first inner layer (7') is a MCrAlX' layer,
wherein X' is at least Yttrium (Y),
especially X' is Y.

6. Layer system according to claim 3 or 5,
wherein the second inner layer (16) is a MCrX'' layer,
wherein X'' is at least silicon (Si) and/or boron (B),
especially X'' is Si and B.

7. Layer system according to claim 4 or 5,
wherein the inner MCrAlX' layer (7) or
the first inner MCrAlX' layer (7')
comprises a NiCrAlY alloy,
especially consists of a NiCrAlY alloy.

8. Layer system according to claim 7,
wherein the inner NiCrAlY layer (7) or
the first inner NiCrAlY layer (7')
comprises in at%:
Ni, 22% Cr, 10% Al, 1.0% Y,
especially consists of Amdry 962.

9. Layer system according to claim 1, 2, 3, 4, 5, 6, 7 or 8,
wherein the chromium-rich layer (10) on the least one MCrX layer (7, 16) comprises an
α-chromium layer,
especially consists of α-Chromium.

10. Layer system according to claim 1, 2, 4, 7, 8, 9,
wherein the chromium-rich layer (10) is
above the lowest MCrAlX' layer (7) and/or
a diffusion layer inside the MCrAlX' layer (7),
especially the chromium-rich layer (10) is only a diffusion layer.

11. Layer system according to claim 1, 3, 6 or 9, wherein the chromium-rich layer (10) is above the second inner layer (16) and/or a diffusion layer inside the MCrX'' layer (16), especially the chromium-rich layer (10) is only a diffusion layer.

12. Layer system according to claim 1, 2, 9 or 10, wherein a first outer MCrX'' layer (13) is present on the chromium rich layer (10), wherein X'' is at least Y, Si and/or B, especially X'' is Y, Si and/or B.

13. Layer system according to claim 6 or 12, wherein the second inner layer (16) or the first outer MCrX'' layer (13) comprises a NiCrSiB layer, which comprises Ni, 17% Cr, 9.2% Si, 0.1% B (in at%). especially consists of NiCrSiB, and very especially consists of Amdry 103.

14. Layer system according to claim 12 or 13, wherein a second outer layer (19) is present on or in the first outer MCrX'' layer (13), which (19) is the outermost layer.

15. Layer system according to claim 14, wherein the second outer layer (19) is an aluminum rich layer, especially an aluminide layer, very especially comprises a β-NiAl structure.

16. Layer system according to claim 12, 13, 14 or 15, wherein the second outer layer (19) is part of an aluminized first outer MCrX'' layer (13).

17. Layer system according to claim 1, 3, 9, 11, 12 or 13,
wherein an outer layer (22) is applied on the chromium rich layer (10),
especially an aluminide layer (22),
very especially a NiAl layer (22),
especially by an aluminized Ni plated layer on the chromium rich layer (10),
especially wherein the Ni layer has a thickness of 10µm to 20µm.

18. Layer system according to claim 4 or 5,
wherein X' is only Y.

19. Laser system according to claim 6 or 12,
wherein X'' is only Si and B.

20. Layer system according to one or more of the preceding claims,
which comprises
a substrate (4)
one or two MCrX layers (7, 7', 16),
a chromium rich layer (10) and
an outer aluminum rich layer (19, 22).

21. Layer system according to one or more of the preceding claims 1 to 20,
which consists of
a substrate (4)
an inner MCrX layer (7)
a chromium rich layer (10)
a first outer MCrX'' layer (13) and
a second outer layer (19).

22. Layer system according to one of the preceding claims 1 to 20,
which consists of
a substrate (4)
an first inner layer (7'),
a second inner layer (16),
a chromium rich layer (10) and
an outer layer (22).

23. Layer system according to any of the preceding claims,
which is heat treated before first use.

24. Layer system according to claim 1, 20, 21 or 22,
wherein the substrate (4) comprises Hastelloy X,
especially consists of Hastelloy X.

25. Layer system according to claim 1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 18, 20, 21 or 22,
wherein M is only Ni.

26. Layer system according to claim 1,
wherein X is only Y, Si, Al or B.

27. Method for producing a component (1)
especially according to any of the claims 1 to 26,
wherein on a substrate (4)
at least one MCrX layer (7, 7', 16) is applied,
especially by HVOF,
wherein X is at least yttrium (Y) and/or silicon (Si) and/or aluminum (Al) and/or boron (B)
and wherein M is nickel (Ni) and/or cobalt (Co) and
wherein a chromium-rich layer (10) is produced,
especially an α-chromium layer (10).

28. Method according to claim 27,
wherein only one MCrX layer (7) is applied on the substrate (4),
which is preferably applied by HVOF.

29. Method according to claim 27,
wherein only two MCrX layers (7', 16) are applied on the substrate (4),
which are preferably applied by HVOF.

30. Method according to claim 29,
wherein a second inner layer (16) is a MCrX'' layer and is applied on the first inner layer (7'),
especially applied by HVOF,
wherein X'' is silicon (Si) and/or boron (B).
especially X'' is silicon (Si) and boron (B).

31. Method according to claim 30,
wherein an stabilizing heat treatment is performed,
preferably at 1010°C and
preferably for 6h.

32. Method according to claim 27, 28, 29, 30 or 31,
wherein the chromium-rich layer (10) is applied by a chromizing treatment,
especially at a temperature between 1050°C and 1080°C,
very especially at 1065°C,
especially for 2h to 4h.

33. Method according to claim 27 or 32,
wherein the chromium-rich-layer (10) is applied by CVD.

34. Method according to claim 27, 32 or 33,
wherein the chromizing is repeated,
especially four times.

35. Method according to claim 27, 32, 33 or 34, wherein a first outer layer (13) is a MCrX'' layer and is applied on the chromium-rich layer (10), especially applied by HVOF, wherein X'' is silicon (Si) and/or boron (B), especially X'' is silicon (Si) and boron (B).

36. Method according to claim 35, wherein a stabilizing heat treatment is performed, preferably at 1010°C and preferably for 6h.

37. Method according to claim 35 or 36, wherein an outer aluminum rich layer (19) is applied, especially by aluminizing.

38. Method according to claim 27, 32, 33 or 34, wherein an outer aluminum rich layer (19, 22) is applied.

39. Method according to claim 38, wherein the outer aluminum rich layer (22) is a Ni-Al- layer (22), especially an aluminide layer (22) and is achieved by plating Nickel and a following aluminizing treatment.

40. Method according to claim 37, 38 or 39, wherein the aluminizing is performed by vapour deposition, especially by CVD.

41. Method according to claim 37, 38, 39 or 40, wherein the aluminizing is performed at 1080°C, especially for 7h.

42. Method according to claim 39,
wherein an stabilizing heat treatment is performed
after plating Nickel (Ni),
preferably at 1120°C and
preferably for 2h and
very preferably in vacuum.

43. Method according to claim 37, 38, 39, 40, 41 or 42,
wherein the layer system is heat treated after
aluminizing,
especially in a vacuum,
very especially at 1080°C for 2h.

FIG 1

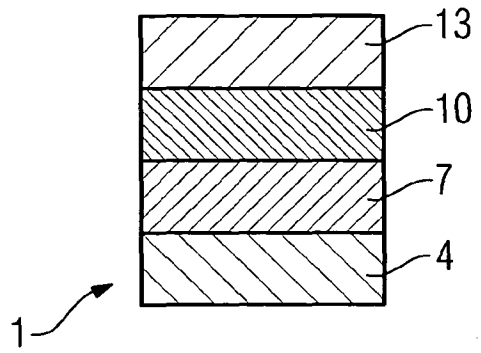


FIG 2

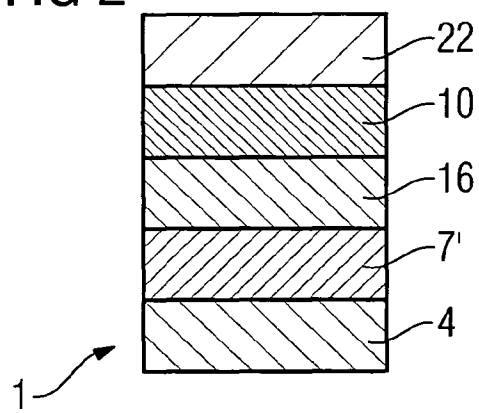


FIG 3

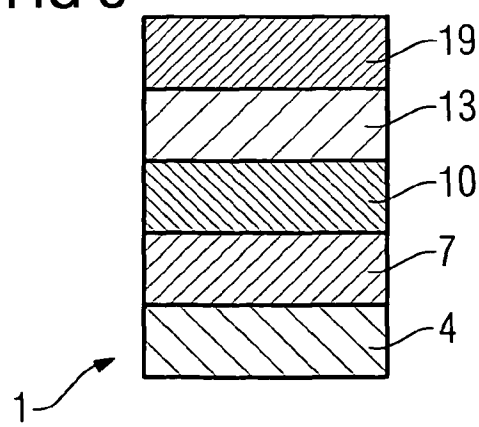


FIG 4

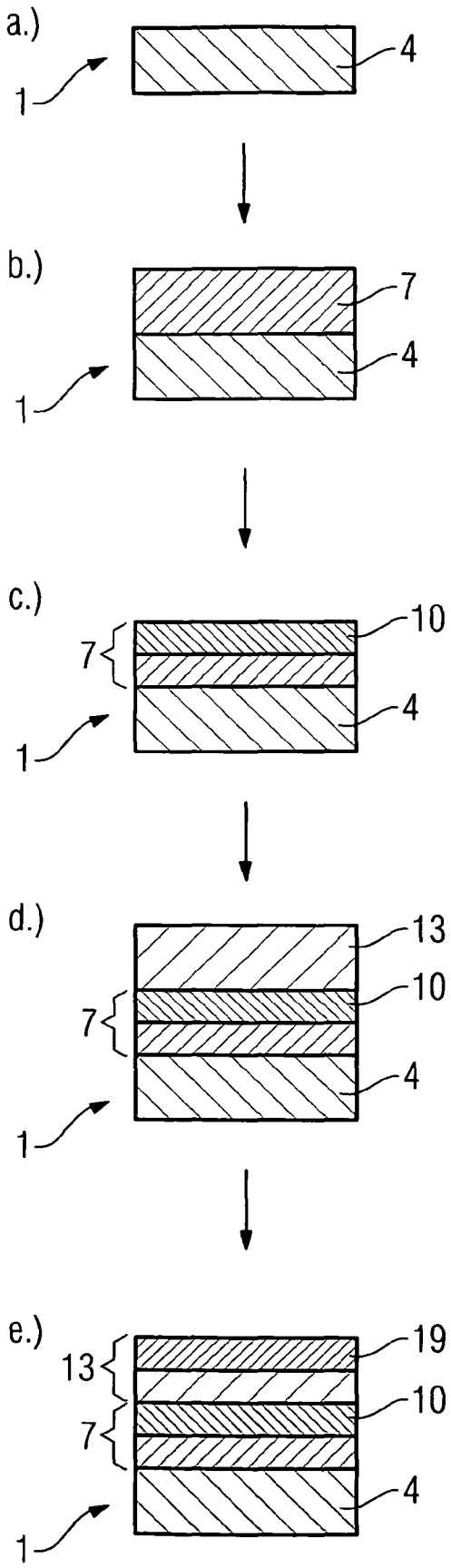
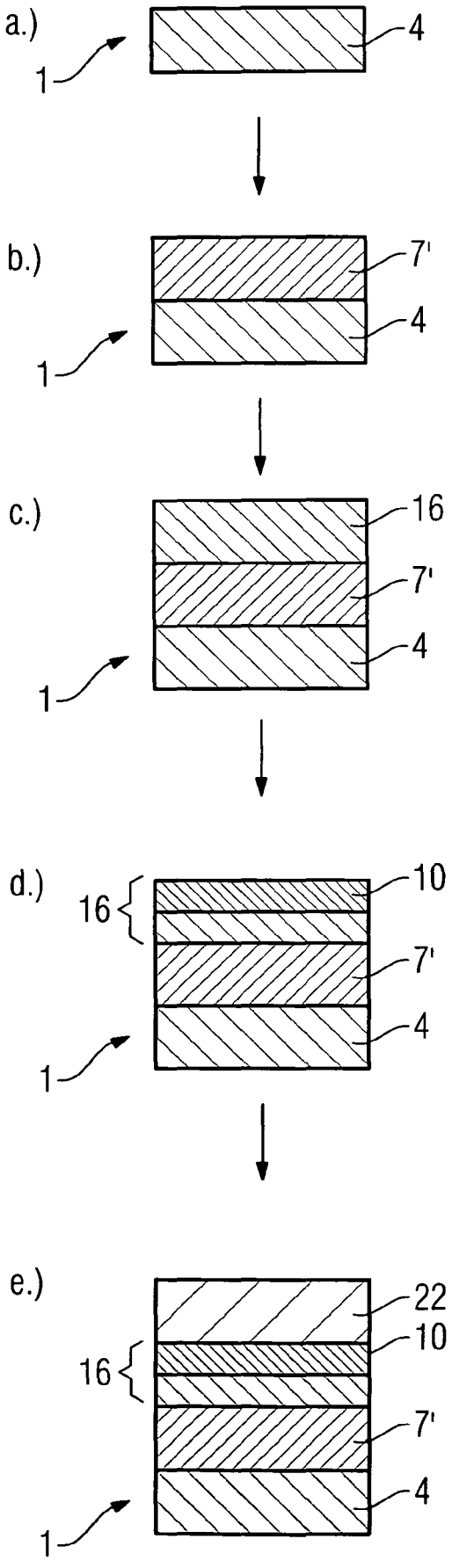


FIG 5



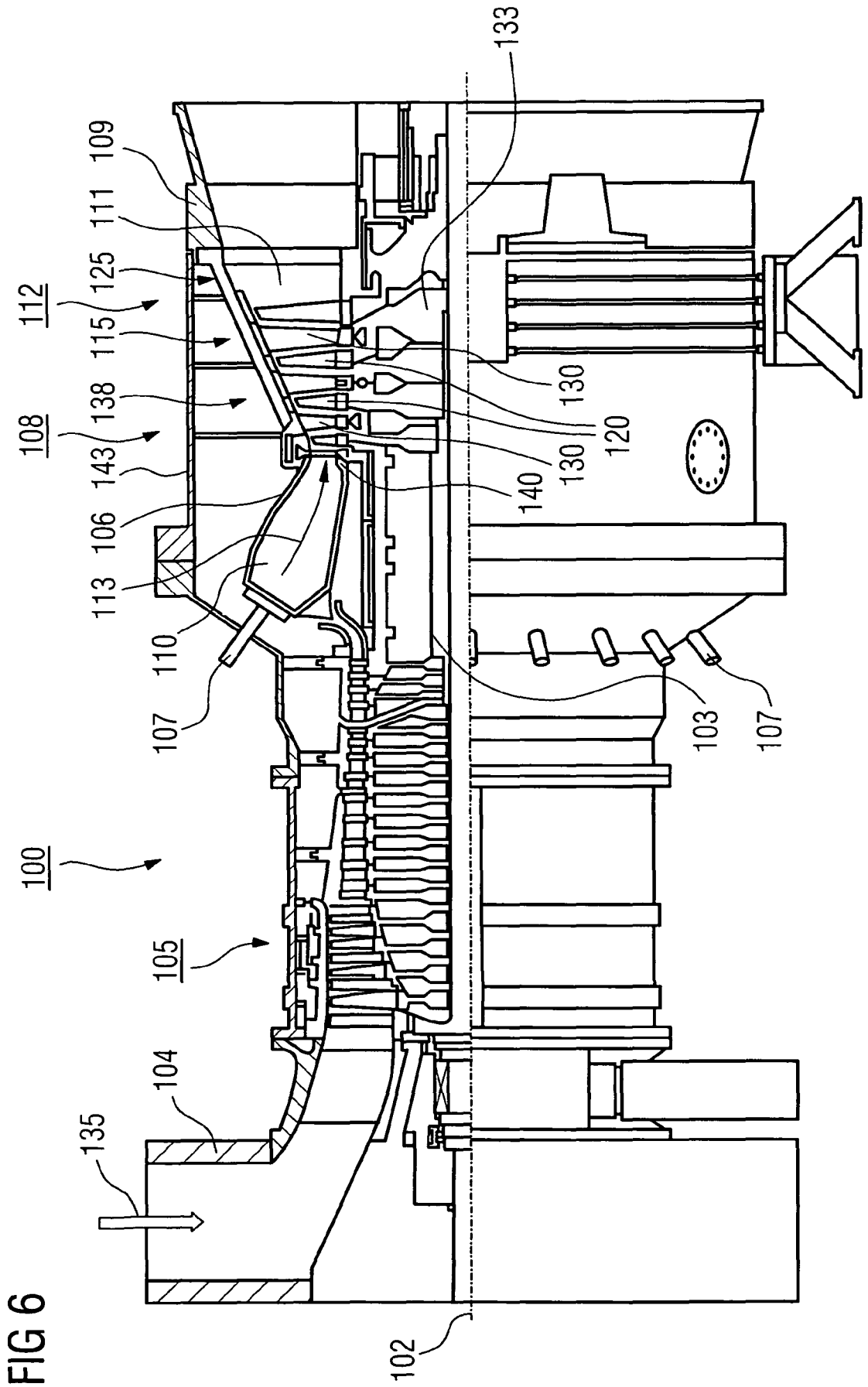

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FIG 6

FIG 7

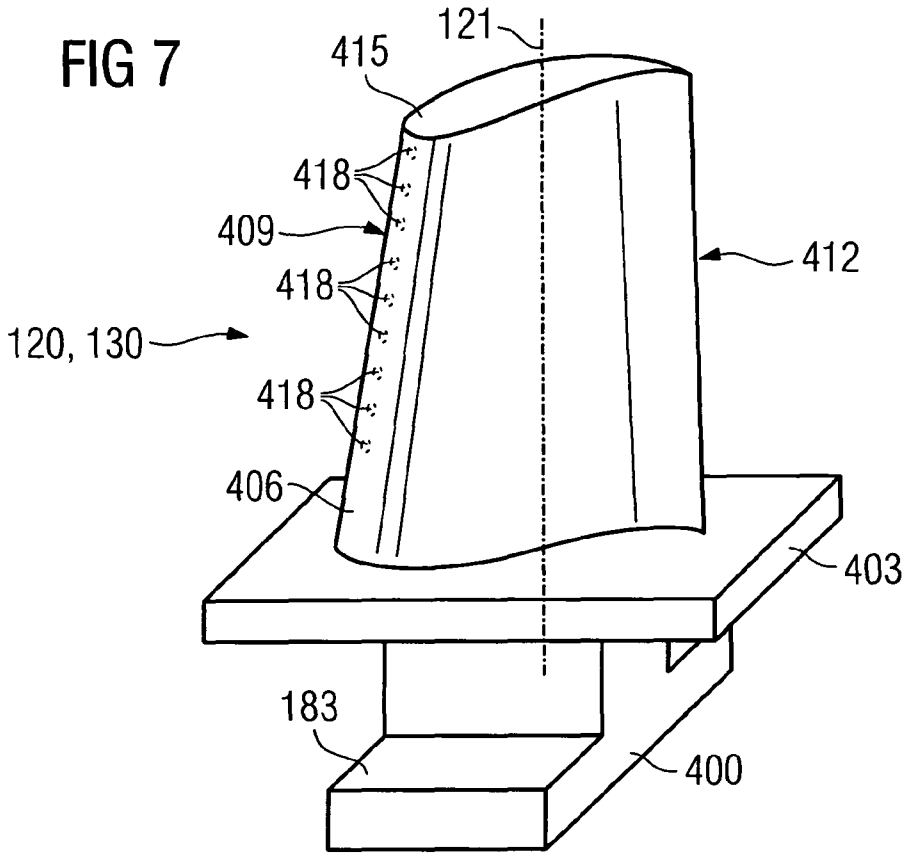
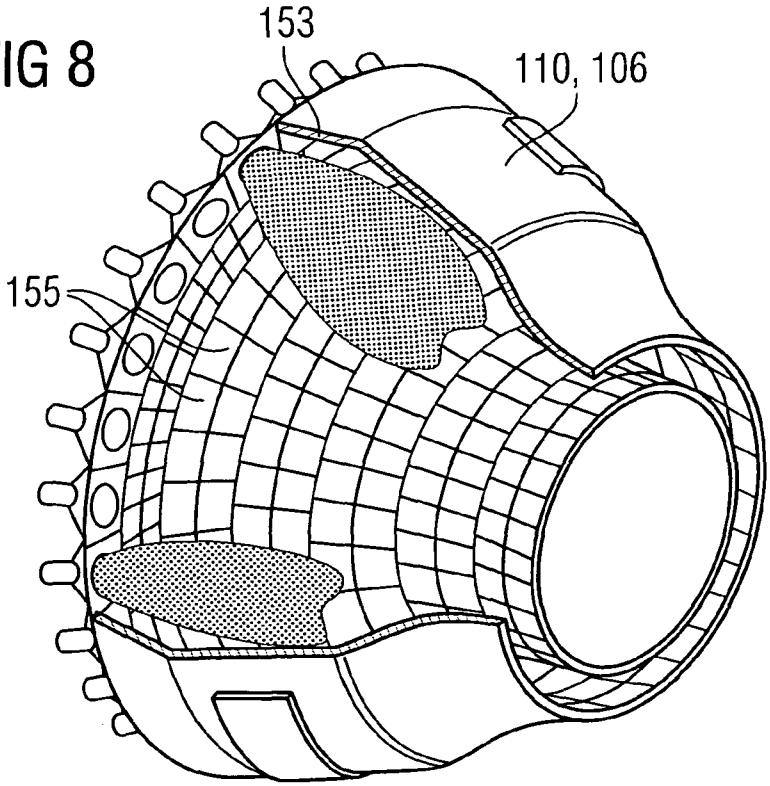

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FIG 8


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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/003204

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C4/18 C23C10/02 C23C28/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 500 252 A (MEELU MEHAR C [GB]) 19 March 1996 (1996-03-19) column 1, line 19 - column 4, line 6 column 6, lines 1-33 column 8, lines 6-12 ----- -/--	1-10, 17-18, 20, 22-30, 32,38, 41,43

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 February 2010	11/02/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chalaftris, Georgios

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/003204

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2005 060243 A1 (MAN TURBO AG [DE]) 21 June 2007 (2007-06-21) claims 1,3 paragraphs [0002], [0008] - [0011], [0017] - [0023]	1-10, 17-18, 20, 22-30, 32-33, 38-41
X	GB 2 322 382 A (ROLLS ROYCE PLC [GB]) 26 August 1998 (1998-08-26) claims 1,2,4,5,12 page 2, line 37 - page 4, line 4 page 7, column 8 - page 1, column 31	1-2,4,7, 17-18, 20, 25-28, 32,38
X	EP 1 676 938 A1 (SIEMENS AG [DE]) 5 July 2006 (2006-07-05) paragraphs [0011] - [0016], [0050]	1-2,4,7, 10,18, 25-28,32
A	US 6 569 492 B2 (FERNIHOUGH JOHN [CH] ET AL) 27 May 2003 (2003-05-27) cited in the application column 4, lines 8-18; claim 1	32,41
A	EP 1 865 150 A1 (SULZER METCO US INC [US]) 12 December 2007 (2007-12-12) paragraphs [0033] - [0035]	8
A	WO 2009/036776 A1 (SIEMENS AG [DE]; KRUSCH CLAUS [DE]; STAMM WERNER [DE]) 26 March 2009 (2009-03-26) page 5, lines 16-23	24
A	EP 1 772 529 A1 (SIEMENS AG [DE]) 11 April 2007 (2007-04-11) paragraphs [0022], [0037]; figure 2 column 3, lines 54-57 column 4, lines 14,15	3,5-6, 22,29-30
A	CA 1 102 184 A1 (ALLOY SURFACES CO INC) 2 June 1981 (1981-06-02) claims 1,3	9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/003204

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5500252 A	19-03-1996	NONE	
DE 102005060243 A1	21-06-2007	CA 2633206 A1	13-09-2007
		CN 101331246 A	24-12-2008
		EP 1969156 A1	17-09-2008
		WO 2007101465 A1	13-09-2007
		JP 2009519398 T	14-05-2009
GB 2322382 A	26-08-1998	NONE	
EP 1676938 A1	05-07-2006	WO 2006072479 A1	13-07-2006
US 6569492 B2	27-05-2003	EP 1162284 A1	12-12-2001
		US 2001053410 A1	20-12-2001
EP 1865150 A1	12-12-2007	CA 2585992 A1	08-12-2007
		CN 101125753 A	20-02-2008
		JP 2007327139 A	20-12-2007
		US 2008124548 A1	29-05-2008
WO 2009036776 A1	26-03-2009	NONE	
EP 1772529 A1	11-04-2007	WO 2007042392 A1	19-04-2007
		US 2009263579 A1	22-10-2009
CA 1102184 A1	02-06-1981	NONE	