

Description

Product for directing a hot, oxidizing gas

The invention relates to a product for directing a hot, oxidizing gas having a surface to be exposed to the gas, which surface is made of an alloy having the following significant proportions by weight: chromium from 10% to 40%, if desired further elements including aluminium from 0% to 20%, silicon from 0% to 10%, reactive elements selected from the group consisting of yttrium, scandium and the rare earth elements, basis at least one element selected from the group consisting of iron, cobalt and nickel.

The invention relates in particular to a product for directing a hot, oxidizing gas, where the gas has properties which are usually present in a waste gas in a gas turbine; in this context, the invention relates particularly to a compound which serves to direct a waste gas in a gas turbine. This component can be a rotor blade or a guide vane, a heat shield or another highly thermally stressed component of a gas turbine. Particularly appropriate is such a component which in operation directs a waste gas having a mean temperature of more than 1000°C, in particular between 1200°C and 1400°C.

The alloy in the product is, in particular, an alloy of the type MCrAlY, where M is the basis of the alloy and is at least one element selected from the group consisting of iron, cobalt and nickel, and where the alloy is further characterized by contents of chromium, aluminium and yttrium or an element equivalent to yttrium, selected from the group consisting of scandium and the rare earth elements. The alloy of the type MCrAlY can also have contents of further elements, for example rhenium.

The invention also relates to a product having a substrate of a nickel-based or cobalt-based superalloy, for example a gas turbine blade or another highly thermally and chemically stressed component of a gas turbine, which component has a protective layer comprising an alloy of the type mentioned.

Substrates for highly thermally and chemically stressed products as are installed, in particular, in gas turbines are preferably made of superalloys based on nickel or cobalt by casting or forging, depending on the superalloy used. In casting such a substrate, it may be possible to resort to a technique which is known as "directional solidification" and gives a substrate having an anisotropic and/or spatially oriented microstructure, in particular a single-crystal microstructure. The superalloys which are generally suitable usually have excellent mechanical properties at the temperatures occurring during operation of the products made therefrom; however, their chemical properties are sometimes such that they require particular measures for protection against corrosion. In order to offer this protection, specific protective layers for superalloys have been developed, in particular the protective layers comprising alloys of the type MCrAlY.

Typical protective layers of such a type are known from EP 0 412 397 A1. This document describes a protective layer having a high corrosion and oxidation resistance, which is characterized by it having a content of rhenium. Specifically, the protective layer has proportions by weight of the following elements: from 1% to 20% of rhenium, from 22% to 50% of chromium, from 0% to 15% of aluminium, where the proportions by weight of chromium and aluminium together are at least 25% and at most 53%, from 0.3% to 2% of yttrium or an element equivalent to yttrium and also from 0% to 3% of silicon. The basis of the alloy forming the protective layer

comprises at least one of the elements iron, nickel and cobalt, plus impurities resulting from the manufacture in the usual proportions by weight. If desired, the protective layer can also contain proportions by weight of the following elements: hafnium up to 5%, tungsten up to 12%, manganese up to 10%, tantalum up to 5%, titanium up to 5%, niobium up to 4% and zirconium up to 2%. The sum of the proportions by weight of these elements should be at most 15%.

Further compositions for protective layers of alloys of the type MCrAlY are described in EP 0 532 150 A1, where nickel is in each case used as basis of the alloy. Apart from the elements cobalt, chromium and aluminium which are always present, suitable additional elements are rhenium, hafnium, yttrium, silicon, zirconium, carbon and boron. In each case, the proportion by weight of aluminium in such an alloy is between 6% and 12%.

US-A 4,451,299 describes protective layers of the type MCrAlY or MCrAlHf (Hf represents hafnium which can, under some circumstances, replace yttrium) having proportions by weight of aluminium between 7% and 20%. Nickel, cobalt and iron or mixtures of at least two of these elements are suitable as bases for the alloys described. In addition, proportions by weight of up to 10% of the elements platinum, rhenium, silicon, tantalum and manganese can be present. The protective layers produced from the alloys are said to be suitable for a temperature range between 650°C and 820°C.

EP 0 207 874 A2 discloses a composition for an alloy containing the following proportions by weight: from 7.5% to 11% of aluminium, from 9% to 16% of chromium, from 2% to 8% of tantalum, from 0% to 25% of cobalt, and whose basis is essentially nickel. Such a protective layer applied to a substrate comprising an appropriately selected superalloy is said to have a particularly high diffusion stability.

The diffusion stability is supposed to comprise the formation between the substrate and the protective layer applied thereto of only a small diffusion zone in which elements from the substrate mix with elements from the protective layer. As a result, at most an insignificant proportion of the aluminium diffuses from the protective layer into the substrate, which could cause the protective layer to lose the capability of forming a film of aluminium oxide on its surface which is essential to the oxidation resistance.

US-A 4,321,310 and 4,321,311 each relate to a product in the form of a gas turbine component comprising a substrate of a superalloy, a metallic protective layer of the type MCrAlY applied thereto and, applied to the latter, a ceramic layer having a columnar crystalline structure, which functions as a thermal barrier layer. This thermal barrier layer makes it possible to increase the thermal stressability of the product, since the thermal barrier layer absorbs a high temperature difference and thus prevents the metallic particles of the product from being excessively stressed. The thermal barrier layer is bound to the product via a thin film of aluminium oxide which is formed by surface oxidation of the metallic protective layer. This surface oxidation can be carried out before or after application of the ceramic layer.

US-A 5,262,245 describes an attempt to modify a superalloy for a product of the type in question in such a way that it is itself capable of forming a thin aluminium oxide film on its surface and thus makes the use of a metallic protective layer for anchoring a ceramic layer, as described above, superfluous.

US-A 3,134,670 relates to corrosion-protected alloys which consist mainly of iron, cobalt or nickel and are characterized by an addition of gallium. The alloys are supposed to be used for producing crowns, fillings and the like in dentistry, and also for producing household articles such as cutlery. The addition of gallium is said to improve the cutting and polishing performance of an alloy without impairing its hardness and toughness. The addition of gallium is also supposed to improve the castability of the alloy and to contribute to the formation of a fine-grained microstructure. There is no suggestion that an alloy described be used at particularly high temperatures.

The formation of a protective oxide film on the surface of the protective layer is an important function for an alloy in the context of a product of the type described in the introduction. Since such an oxide film steadily wears off during operation, it requires continual renewal. This renewal occurs by means of continual oxidation of aluminium which diffuses from the protective layer to the surface, reacts there with oxygen and thus supplements the film. The maximum life of a protective layer is accordingly determined by its aluminium content, since with the loss of aluminium the protective layer loses the capability of forming the protective oxide film, and thus loses its protective action. Thus, a high aluminium content in an alloy for a protective layer is desired in order to give a long life.

However, a high aluminium content leads to embrittlement of the alloy. This is because the aluminium is not stored in the alloy in elemental form, but at least a significant proportion is present in the form of intermetallic compounds, in particular intermetallic compounds of nickel and aluminium or cobalt and aluminium.

Accordingly, the aluminium content in an alloy to be used as a protective layer has to be restricted to a particular level. This level is determined by many factors, and additions of elements such as rhenium can
5 increase the maximum possible proportion by weight of aluminium in an alloy. As a general guideline, a proportion by weight of aluminium of 15% can be regarded as an upper limit. Such a proportion by weight does require very careful measures for matching the contents of the
10 other elements in the protective layer so as to keep its brittleness within acceptable limits.

Problems similar to those for aluminium also occur in the case of the element silicon which is known as a constituent of protective layers and which likewise
15 can develop a protective oxide film on an alloy. High additions of silicon also embrittle an alloy so that the proportion by weight of silicon also may not exceed a certain limit. The proportion by weight of silicon is usually kept less than 1%.

20 In view of the problems indicated, it is an object of the invention to provide an alternative to the products known and tested hitherto for directing hot, oxidizing gases, with the alloy used retaining the advantages achievable by addition of aluminium and/or
25 silicon, particularly the capability of forming a protective oxide film, but avoiding the danger of embrittlement which was always present for the compositions known hitherto.

This object is achieved according to the invention
30 tion by a product for directing a hot, oxidizing gas having a surface to be exposed to the gas, which surface is made of an alloy having the following proportions by weight:

Chromium from 10% to 40%
Gallium from 1% to 20%
Aluminium from 0% to 20%
Silicon from 0% to 10%

5 a reactive element selected from the group consisting of yttrium, scandium and the rare earth elements

from 0% to 2%

Hafnium from 0% to 5%

Manganese from 0% to 10%

10 Niobium from 0% to 4%

Platinum from 0% to 10%

Rhenium from 0% to 20%

Tantalum from 0% to 10%

Titanium from 0% to 5%

15 Tungsten from 0% to 12%

Zirconium from 0% to 2%

basis at least one element selected from the group consisting of iron, cobalt and nickel.

20 The presence in the alloy of the usual proportions of the usual impurities resulting from the manufacture has to be expected. Examples of such impurities are, without claiming to be exhaustive, phosphorus and sulphur.

25 The addition according to the invention of gallium to an alloy can ensure a desired oxidation resistance, with the gallium completely or partially replacing the aluminium or silicon always required hitherto. This gives an alloy which, at a proportion by weight of aluminium of significantly below 15%, can have
30 an oxidation resistance corresponding to the oxidation resistance of a known alloy having a proportion by weight of aluminium of more than 15%, while the ductility (the opposite of "brittleness") of the gallium-containing alloy is significantly better.

Like aluminium and silicon, gallium is able to form a protective film of firmly adhering oxide on a surface of the alloy when this surface is exposed to oxygen, possibly at elevated temperature. An advantage here is the close chemical similarities of gallium to aluminium and silicon. Gallium forms a very stable oxide (Ga_2O_3) having an enthalpy of formation of -1815 kJ/mol . For aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2) this enthalpy of formation is -1675 and -860 kJ/mol respectively. In addition, the melting point of gallium oxide is very high at 1725°C and comparable to the melting point of aluminium oxide at 2045°C and silicon oxide at 1713°C .

Gallium forms intermetallic compounds with nickel, in particular an intermetallic compound NiGa which in all relevant properties resembles corresponding intermetallic compounds of nickel and aluminium; formation of intermetallic compounds of nickel, gallium and aluminium, for example NiGaAl , may also occur. For chemical systems containing cobalt and gallium and possibly aluminium, similar proportions are to be expected owing to the great chemical similarity of cobalt and nickel; for systems containing iron and gallium and possibly aluminium, comparable proportions can also be reckoned with. In each case, the gallium which is very volatile in pure form can be incorporated into the alloy as an intermetallic compound and thus can be available even at elevated temperatures for forming a stable oxide on the surface of the alloy.

The proportion by weight of chromium in the alloy of the invention is between 10% and 40%.

The proportion by weight of aluminium in the alloy which forms the surface of the product of the invention is preferably up to 10%. This ensures, in particular,

that no undesired embrittlement of the alloy by the aluminium can result.

For considerations analogous to those just mentioned, the proportion by weight of silicon in the alloy of the product of the invention is preferably limited to a value of up to 2%.

It is likewise preferred that the alloy of the product has a content of a reactive element selected from the group consisting of yttrium, scandium and the rare earth metals. The action of such reactive elements is well known from practical use of MCrAlY alloys and is also expected in a comparable manner for the alloy in the present context. The reactive element is preferably yttrium and its proportion by weight is up to 2%.

It is likewise preferred that the basis contains cobalt and/or nickel, but not iron. This too is known from relevant practical use of the MCrAlY alloys.

Furthermore, the alloy of the product preferably has a content of aluminium so that both gallium and aluminium produce an effect. The proportion by weight of aluminium is preferably up to 10% since the gallium at least partially aids and supplements the action of the aluminium. In this context, the proportion by weight of aluminium is still preferably greater than the proportion by weight of gallium, with the sum of the proportions by weight of aluminium and gallium preferably being up to 20%.

It is generally preferred that the proportion by weight of gallium in the alloy is up to 15%.

Preference is also given to an embodiment of the product in which the alloy has a content of rhenium.

The proportion by weight of rhenium is in particular up to 20%, preferably up to 15%.

Another embodiment of the product is distinguished by having a surface which is covered by a film
5 consisting at least partly of gallium oxide.

A particularly preferred embodiment of the product is distinguished by an alloy having a basis of nickel and proportions by weight of the following elements: cobalt from 5% to 20%, chromium from 20% to
10 30%, aluminium from 5% to 12%, gallium from 3% to 8%, yttrium from 0.2% to 1% and rhenium from 0% to 5%. The presence of impurities resulting from manufacture in the usual proportions by weight is of course to be taken into account; contents of further elements and additives are
15 also possible.

A particularly preferred composition of the alloy just described is distinguished by the following proportions by weight: cobalt from 8% to 16%, chromium from 21% to 27%, aluminium from 6% to 10%, gallium from 4% to 6%,
20 yttrium from 0.4% to 0.8% and rhenium from 2% to 4%.

Each of the alloys described can additionally contain further elements, in particular: hafnium from 0% to 5%, tungsten from 0% to 12%, manganese from 0% to 10%, tantalum from 0% to 5%, titanium from 0% to 5%, niobium
25 from 0% to 4% and zirconium from 0% to 2%.

The alloy in the product is preferably a protective layer of a metallic substrate, in particular on a substrate comprising a nickel-based or cobalt-based superalloy. The substrate is here, in particular,
30 a component for directing a hot, oxidizing gas, in particular in a gas turbine.

On the protective layer of the product, a further gas-permeable ceramic layer is preferably applied, with this ceramic layer having, in particular, a micro-structure composed of columnar crystals. Such a ceramic layer is provided, in particular, as a thermal barrier layer for a product in the form of a component for a gas turbine, where the product during operation is exposed to a temperature which significantly exceeds 1000°C and, depending on the application, can extend to just below the melting point of the substrate. The ceramic layer preferably comprises a partially stabilized zirconium oxide, i.e. a material which contains not only zirconium oxide as main constituent but also another oxide, for example lanthanum oxide, cerium oxide, calcium oxide, yttrium oxide or magnesium oxide. The incorporation of the other oxide stabilizes the crystalline structure of the zirconium oxide and prevents the zirconium oxide from undergoing, when heated, a phase transition in which the crystalline structure of the zirconium oxide changes considerably. In addition, the ceramic layer preferably adheres to a film adhering to the surface and containing gallium oxide, which film is formed by oxidation of the alloy prior to or after application of the ceramic layer.

For the substrate on which the alloy is to be applied, preference is given to a composition based on nickel and additional elements in the following proportions by weight: from 0.06% to 0.14% of carbon, from 10% to 20% of chromium, from 6% to 11% of cobalt, from 1% to 3% of molybdenum, from 1% to 6% of tungsten, from 1% to 6% of tantalum, from 0% to 2% of niobium, from 1% of 6% of aluminium, from 1% to 6% of titanium, from 0% to 0.3% of boron and from 0% to 0.2% of zirconium.

A description of a preferred illustrative embodiment of the invention is given below:

On a substrate in the form of a thermally, mechanically and corrosively highly stressed component of a gas turbine, in particular a turbine blade for a gas turbine which in operation is exposed to a hot waste gas having a temperature of 1300°C or more, there is applied an alloy as protective layer, with the application being carried out by vacuum plasma spraying followed by customary further treatments. The alloy has a basis of nickel and additionally contains the following proportions by weight: 10% of cobalt, 23% of chromium, 8% of aluminium, 5% of gallium, 3% of rhenium and 0.6% of yttrium. The substrate comprises a nickel-based superalloy of a conventional type; such superalloys are known by the designations IN 738 and PWA 1483.

Apart from vacuum plasma spraying, other possible ways of applying the protective layer are the various processes known per se of physical vapour deposition (PVD) or chemical vapour deposition (CVD). In particular, a PVD process is used for applying a ceramic layer onto the protective layer.

It is expected that during operation when the protective layer is exposed to a waste gas containing oxygen the protective layer becomes coated with a film which consists at least partially of gallium oxide. In addition, it is expected that if the protective layer has a significantly increased life it has a significantly increased ductility compared with a protective layer which contains no gallium but instead a correspondingly increased proportion by weight of aluminium. This makes the gallium-containing protective layer significantly less susceptible to crack formation, which has an additional very positive effect on its life.

As a result of the addition of gallium, a significantly increased alloy life is expected in comparison with the alloys of the prior art. If the thermal stress on the product is very high during operation, the surface formed by the alloy can be

coated with a ceramic layer, preferably a ceramic layer having a microstructure composed of columnar crystals and comprising partially stabilized zirconium oxide. In particular, the layer is here bound to a film containing
5 gallium oxide and formed by oxidation of the alloy, which film adheres to the surface.



Claims

1. Product for directing a hot, oxidizing gas having a surface to be exposed to the gas, which surface is made of an alloy having the following by weight:
- 5 Chromium from 10% to 40%
Gallium from 1% to 20%
Aluminium from 0% to 20%
Silicon from 0% to 10%
a reactive element selected from the group consisting of
10 yttrium, scandium and the rare earth elements,
from 0% to 2%
Hafnium from 0% to 5%
Manganese from 0% to 10%
Niobium from 0% to 4%
15 Platinum from 0% to 10%
Rhenium from 0% to 20%
Tantalum from 0% to 10%
Titanium from 0% to 5%
Tungsten from 0% to 12%
20 Zirconium from 0% to 2%
basis at least one element selected from the group consisting of iron, cobalt and nickel.
2. Product according to Claim 1, wherein the proportion by weight of aluminium is up to 10%.
- 25 3. Product according to Claim 1 or 2, wherein the proportion by weight of silicon is up to 2%.
4. Product according to any of the preceding claims, wherein the reactive element is yttrium and its proportion by weight is up to 2%.
- 30 5. Product according to any of the preceding claims, wherein the alloy contains as basis only cobalt and/or nickel.



6. Product according to any of the preceding claims, wherein the alloy contains aluminium.
7. Product according to Claim 6, wherein the proportion by weight of aluminium is greater than the proportion by weight of gallium.
8. Product according to Claim 6 or 7, wherein the sum of the proportions by weight of aluminium and gallium is up to 20%.
9. Product according to any of the preceding claims, wherein the proportion by weight of gallium is up to 15%.
10. Product according to any of the preceding claims, wherein the proportion by weight of rhenium is up to 15%.
11. Product according to any of the preceding claims, wherein the surface is covered by a film consisting at least partially of gallium oxide.
12. Product according to any of the preceding claims, wherein the basis of the alloy is nickel and the alloy has the following proportions by weight:
- | | |
|-----------|-----------------|
| Cobalt | from 5% to 20% |
| Chromium | from 20% to 30% |
| Aluminium | from 5% to 12% |
| Gallium | from 3% to 8% |
| Yttrium | from 0.2% to 1% |
| Rhenium | from 0% to 5%. |
13. Product according to Claim 12, wherein the alloy has the following proportions by weight:
- | | |
|-----------|--------------------|
| Cobalt | from 8% to 16% |
| Chromium | from 21% to 27% |
| Aluminium | from 6% to 10% |
| Gallium | from 4% to 6% |
| Rhenium | from 2% to 4% |
| Yttrium | from 0.4% to 0.8%. |



14. Product according to any of the preceding claims, wherein the alloy is applied as protective layer to a metallic substrate, in particular a substrate comprising a nickel-based or cobalt-based superalloy.
- 5 15. Product according to Claim 14, wherein a gas-permeable ceramic layer, in particular one having a microstructure composed of columnar crystals, is applied to the surface.
- 10 16. Product according to Claim 15, wherein the ceramic layer comprises a partially stabilized zirconium oxide.
17. Product according to Claim 15 or 16, wherein the ceramic layer adheres to a film adhering to the surface and containing gallium oxide.
- 15 18. Product according to any of Claims 14 to 17, wherein the substrate is based on nickel and has the following proportions by weight:
- | | | | | | |
|----|------|-------|----|-------|---------------|
| | from | 0.06% | to | 0.14% | of carbon |
| | from | 10% | to | 20% | of chromium |
| 20 | from | 6% | to | 11% | of cobalt |
| | from | 1% | to | 3% | of molybdenum |
| | from | 1% | to | 6% | of tungsten |
| | from | 1% | to | 6% | of tantalum |
| | from | 0% | to | 2% | of niobium |
| 25 | from | 1% | to | 6% | of aluminium |
| | from | 1% | to | 6% | of titanium |
| | from | 0% | to | 0.3% | of boron |
| | from | 0% | to | 0.2% | of zirconium. |