

EUROPEAN QUALIFYING EXAMINATION 2021

Paper A

This paper comprises:

- | | | |
|---|-----------------------------|-----------------|
| * | Letter from the applicant | 2021/A/EN/1-7 |
| * | Drawings of the application | 2021/A/EN/8-9 |
| * | Document D1 | 2021/A/EN/10-12 |
| * | Document D2 | 2021/A/EN/13-14 |

Letter from the applicant

Generate Ltd.
Parsons Green
5 United Kingdom

Dear Ms Laval,

10 [001] Our company has recently been founded to develop and manufacture components
that are used in gas turbine engines. We intend to present our latest range of products
at a trade fair in South Africa tomorrow and wish to ensure that the relevant technology
is protected by a patent application. A potential customer has invited us on a safari for
the rest of today in a zone which has no mobile phone coverage and so we will not be
15 available for questions. I have enclosed all the necessary information that you will need
to draft the patent application and two documents, D1 and D2, that may be interesting.
Please note that it is company policy not to pay additional claims fees.

[002] A typical gas turbine, such as that used in aircraft engines, consists of three
20 stages. The first stage is a compressor in which air is compressed to a high pressure.
The second stage is the combustion zone where the high-pressure air and fuel are
mixed and combusted. The third stage is the exhaust section and uses the energy of the
hot exhaust gas coming from the combustion zone to provide propulsion for the aircraft
and the energy needed by the compressor.

[003] The efficiency of a gas turbine is improved when the temperature of the combustion zone is as high as possible. The combustion zone therefore needs to be constructed from materials able to withstand these high temperatures. Engine components used in the combustion zone are typically made from superalloys (a well-known class of cobalt and nickel alloys specially adapted for use at high temperatures). Modern gas turbines, however, are designed to operate with a combustion zone having a temperature of at least 1 600°C, which is above the melting point of superalloys. It is therefore necessary to protect the superalloy against such high temperatures. One approach is to use a thermally insulating layer of a ceramic oxide, which is often zirconium oxide. Another approach used only for turbine blades is to provide holes through the component and to cool it with air flowing through the holes. This kind of air cooling is able to cool the component, but is usually not sufficient on its own.

[004] Superalloy engine components coated with zirconium oxide are effective, but only have a limited lifetime. The coefficients of thermal expansion of superalloys and zirconium oxide differ significantly. Therefore when a coated superalloy engine component is heated the superalloy expands by a different amount than the coating. This leads to stress at the interface between the superalloy and the coating, and eventually parts of the coating will fall off. The component then needs to be replaced. One known solution to this problem is to use an adhesion layer containing nickel and/or cobalt and 10-50 wt.% aluminium between the ceramic oxide and the superalloy. A coated engine component with a coating improved in this manner is shown in document D1. The lifetime of the components of document D1 is improved, but further improvements are needed.

[005] We have now developed a new type of coated engine component in which a substrate is coated with a ceramic oxide layer having a columnar microstructure. The spaces between the columns allow the coating to deform when the substrate and the ceramic oxide expand upon heating and much less stress is generated. The columns
5 must be orientated substantially perpendicularly to the surface to provide this effect. A column is considered to be substantially perpendicular if the angle between the column and the surface of the substrate is between 75 and 105°. This new type of coated engine component can be made using the known adhesion layer and the known ceramic zirconium oxide layer. In this case the lifetime of the coated component will significantly
10 increase. It is also possible to omit the adhesion layer and deposit the ceramic oxide directly on the component. Such a component will have a lifetime similar to the components known from document D1 but will weigh less, an important advantage if the component is to be used in aircraft engines. It has surprisingly been found that the protection of superalloys against high temperatures is just as good with the ceramic
15 oxide layer having a columnar microstructure as with conventional ceramic oxide layers.

[006] The type of ceramic oxide used is not critical and may be selected from the class of ceramic oxide materials disclosed in document D1. Examples of these materials are zirconium oxide, aluminium oxide or titanium oxide. The ceramic oxide layer preferably
20 has a thickness of at least 25 micrometres, otherwise thermal insulation is insufficient. The thickness usually does not exceed 2 millimetres. A maximum thickness of 2 millimetres is preferred to ensure that the weight of the component is not too high. The adhesion layer is made from the materials used in document D1 and typically has a thickness of 10-200 micrometres.

[007] The following figures illustrate the invention:

Fig. 1 shows a cross section of a coated component made using electron-beam evaporation.

Fig. 2 shows a cross section of a coated component made using spraying followed by
5 laser treatment.

Fig. 3 shows a turbine blade with cooling holes.

[008] One of the inventors carried out a study on the thermal properties of an engine component from a hot part of a bus engine consisting of a metal coated with a ceramic
10 oxide, namely aluminium coated with a 30-micrometre-thick aluminium oxide layer. The aluminium oxide layer used had a columnar microstructure with columns perpendicular to the surface of the engine component. The inventor identified properties that he believed could be useful for turbine components. Aluminium itself does not withstand the temperature of the combustion zone of turbines, even when coated. In addition,
15 anodisation, the method used to make the columnar structure in this study, does not form columnar coatings on any other metal. Therefore, a different coating method was needed. The inventors have investigated electron beam evaporation, a coating technique known from document D2. They identified the conditions needed to deposit a useful thermally insulating layer of a ceramic oxide with a columnar microstructure on an
20 engine component made from a superalloy.

[009] Electron-beam evaporation is a known method for depositing ceramic oxide layers on components. It is also known to evaporate ceramic oxides using a plasma. Suitable apparatus are commercially available, see for example document D2. In order to deposit evaporated material as a coating on a superalloy component, the component has first to
5 be fixed to a holder and placed in a vacuum chamber along with a source of the ceramic oxide and, if necessary, a source for the adhesion layer. The vacuum chamber is then evacuated. In a typical process the component in the evacuated vacuum chamber is continuously rotated and then heated to the temperature at which the evaporated material will be deposited. The material for the adhesion layer, if used, is evaporated
10 and deposits on the component, which for the adhesion layer usually happens at a temperature of 800-900°C. The ceramic oxide is then deposited on the adhesion layer or directly on the component if no adhesion layer is used. We have established that a columnar structure is only obtained, when using an evaporation method, if an electron beam is used to evaporate the ceramic oxide and when the temperature of the
15 component during the deposition of the ceramic oxide is 920-1 050°C. When the ceramic oxide is zirconium oxide a temperature of 950-1 000°C is required.

[010] A cross section through a preferred coating formed using the above method is shown in Fig. 1. The component 10 comprises a substrate 11 made of a superalloy, an
20 adhesion layer 12 and a ceramic oxide layer 13. The structure of the ceramic oxide layer is columnar, having columns 14a, 14b, 14c with spaces 15a, 15b between the columns.

[011] We have also discovered a further method that can be used to make the coated components of the invention. In this method a conventional coating is made, for example, using the method described in document D1 and then the coating is machined, preferably with a laser, to form the columns in the ceramic oxide layer. Preferably the ceramic oxide layer and the adhesion layer if present are both deposited by plasma spraying and a laser is used to form the columnar structure. This method is advantageous because a conventional coating apparatus can be used.

[012] A cross section through a coating made according to this method is shown in Fig. 2. The coated component 20 in this figure includes a superalloy substrate 21, an adhesion layer 22, and a ceramic oxide layer 23. Columns 24a, 24b and a space 25 between the columns are also shown. The individual columns of the coating of this embodiment consist of a stack of flattened grains 26a, 26b, 26c of ceramic oxide, due to the plasma spraying used to make the coating. The lifetime of the coating made using this method is improved over known coatings, but not as good as the lifetime of coatings made by electron-beam evaporation.

[013] The coated engine component according to the invention may be a turbine component, such as a turbine blade or a lining of a combustion chamber. Coated engine components according to the invention may also be parts of pumps used in rocket engines or other engine components that are to be used at very high temperatures, such as the lining of the exhaust section of a gas turbine engine. Components with a ceramic oxide having a columnar microstructure cannot be used in technical areas other than in engine components for engines with a combustion zone at a temperature of at least 1 600°C.

[014] One particularly preferred embodiment of the invention is to combine the inventive coating with air cooling. Air cooling in turbine blades is achieved by making the turbine blade hollow and passing cooling air from the hollow centre of the turbine blade to its exterior surface through holes provided in the walls and any coating present. Fig. 3

5 illustrates a turbine blade 30 with cooling holes 31a, 31b, 31c. The most convenient method for making this embodiment is the second method as the laser used to make the columnar structure can also be used to drill through both the coating and the walls of the turbine blade to make the cooling holes.

10 Yours sincerely,
Alexandre Burdin

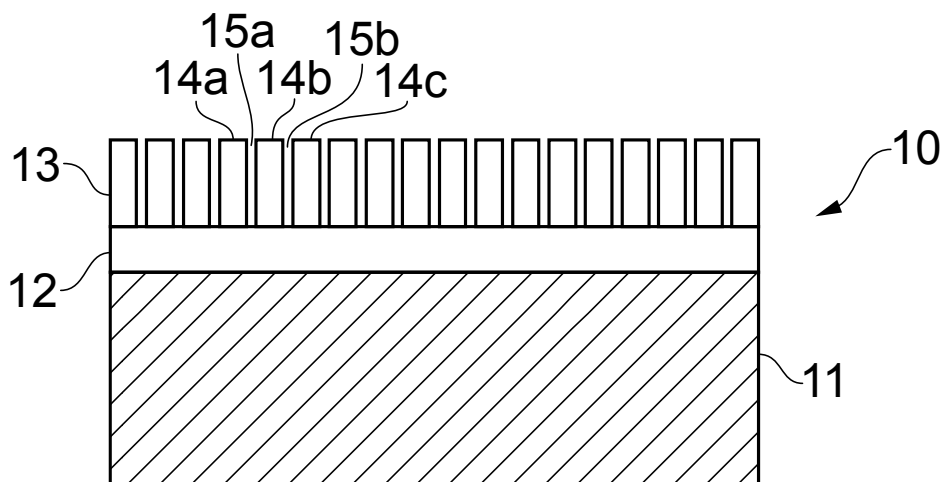


FIG. 1

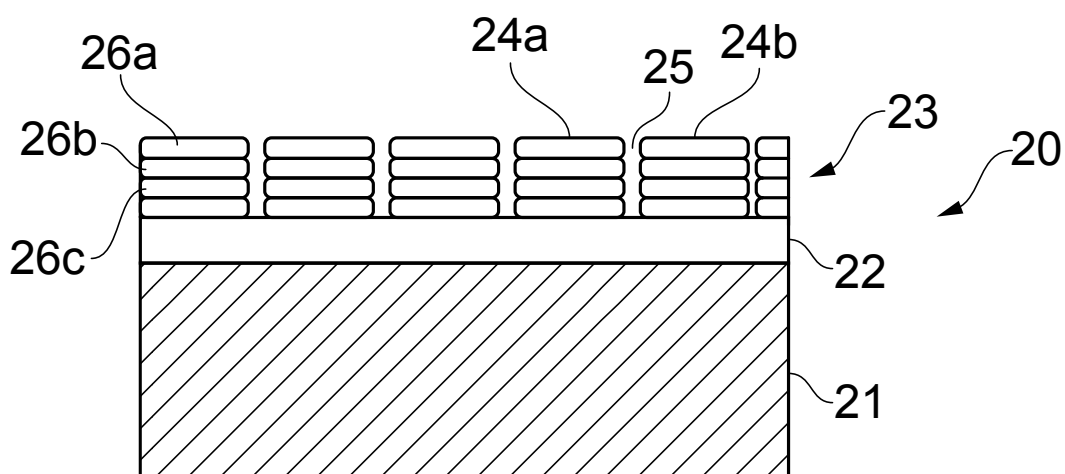


FIG. 2

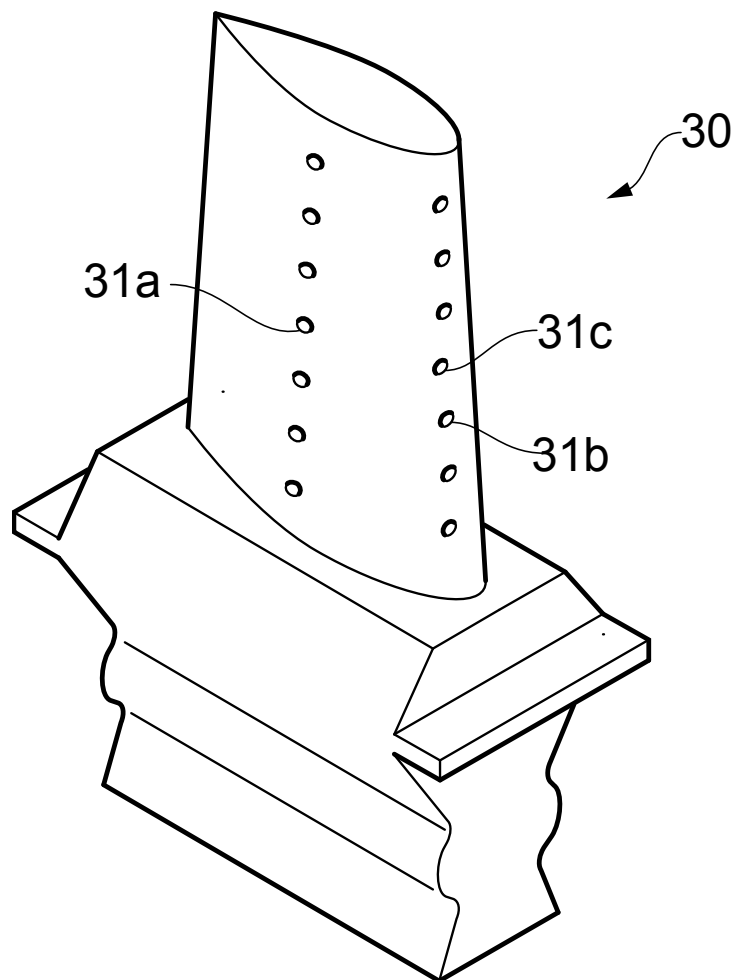


FIG. 3

Document D1

Patent application EP-A 5 000 002, dated 1st of March 2014

Coated Turbine Blade with Extended Lifetime

5

[001] Turbine blades used in the hottest parts of turbine engines are made from superalloys. The surface of the blade is typically coated with a ceramic oxide to protect it against the high temperatures present in the engine.

- 10 [002] The term ceramic oxide is used by different turbine manufacturers to refer to different groups of materials. In the present application the term refers to metal oxides that melt at a temperature higher than 1 600°C. This temperature is the minimum operating temperature for the combustion zone of modern turbine engines. Metal oxides melting at lower temperatures are unable to provide sufficient thermal insulation. The
- 15 ceramic oxide most commonly used is zirconium oxide, but aluminium oxide and complex oxides with a pyrochlore structure are also effective. Coated turbine blades have been available for a number of years. It has been determined that the components needed to be replaced more often than anticipated because the coating had peeled off. This is believed to be due to the difference between the coefficient of thermal expansion
- 20 of the coating and that of the superalloy. This difference results in stress as the component heats up and cools down again, and over a number of such cycles can lead to loss of the coating.

[003] The invention concerns a new type of coated turbine blades. The turbine blade according to the invention is first coated with a layer of material that has a coefficient of thermal expansion with a value between that of the superalloy from which the turbine blade is made and that of the ceramic oxide. This intermediate adhesion layer is
5 composed of a nickel or cobalt alloy. Preferably a nickel alloy is used if the superalloy substrate is also nickel-based. The alloy further contains 10-50 wt.% of aluminium and up to 25 wt.% of chromium and/or yttrium. The turbine blade is then coated with a conventional ceramic oxide coating at least 25 micrometres thick.

10 [004] Both the adhesion coating and the ceramic oxide are preferably applied by plasma spraying. This technique results in a uniform coating structure consisting of flattened grains of the coating material with some porosity. The fact that the structure is uniform is believed to be favourable. If desired, the surface of the coated component can be melted with a laser, this results in a surface better able to withstand erosion.

15 [005] The coating structure is illustrated in Fig. 1, which shows a cross section through a turbine blade. The turbine blade comprises a superalloy substrate 10, an intermediate adhesion layer 20 and a top layer of a ceramic oxide 30. In a series of tests a turbine blade having a coating with an intermediate layer has its lifetime increased by 40% as
20 compared to a coated turbine blade without the intermediate layer.

Claims

1. A turbine blade comprising a superalloy substrate, an adhesion layer on the surface of the substrate and a ceramic oxide layer on the surface of the adhesion layer.

2. A turbine blade in accordance with claim 1 wherein the adhesion layer is a nickel or
25 cobalt alloy containing 10-50 wt.% of aluminium and up to 25 wt.% of chromium or yttrium.

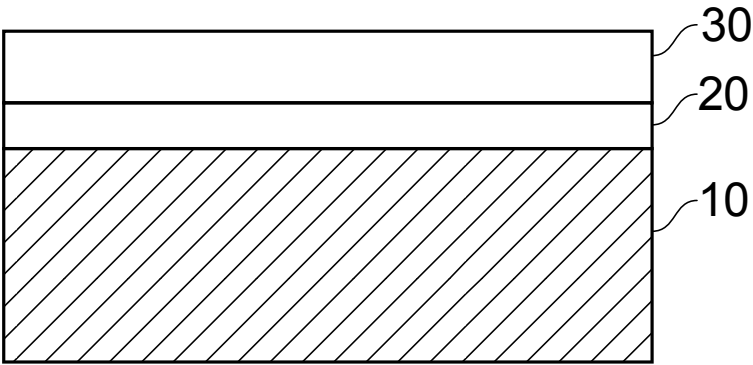


FIG. 1

Document D2

Sales catalogue dated 23rd of March 2002

- 5 [001] Zirvap™ is the latest generation of flexible electron-beam evaporation coating apparatus. The apparatus has been specially designed for depositing layers of ceramic oxides onto metals. Our patented coating chamber design is modular and the number of modules required will depend on the component being coated.
- 10 [002] Electron-beam evaporation is a very efficient method for coating ceramic oxide layers onto metals. In this technique a ceramic oxide target is irradiated with an electron beam. The electron beam locally heats the target to temperatures of over 2 000°C, evaporating the ceramic oxide. The vapour generated flows towards the component to be coated and condenses on the relatively cold component forming the desired layer.
- 15 The component can be rotated or stationary, and the integrated heating module can provide component temperatures of from room temperature to 1 200°C. The temperature of the component controls the microstructure of the layer. The coating chamber needs to be under vacuum to perform the process and the pressure can be varied in our coating chamber. A very low pressure is useful when high coating speeds
- 20 are needed. Higher pressures are useful when low coating speeds are needed.
- [003] The coating chamber can be supplied with slots for up to eight targets of coating material and up to four electron beams. Thus, even large components can be rapidly coated with a thick coating. Alternatively, a multi-layered coating can be deposited in a
- 25 single coating apparatus.

[004] The coating apparatus has successfully been employed to provide a security coating on a turbine blade made from a superalloy. Such security coatings are used to guard against counterfeit components. A very thin (approx. 1 micrometre) layer of zirconium oxide is deposited on the base of the turbine blade at 950°C. This coating has

5 a columnar microstructure with columns perpendicular to the component surface and gaps between the columns. The gaps can be loaded with a unique blend of rare earth ions. The customer can identify this blend and thus confirm that the component is authentic. If desired, the coating can be removed with a plasma before the component is used.

10

[005] Contact us today at Zirvapsales@beamcoat.com and let us help you fulfil all your coating needs.