

Description

The present invention concerns a process for producing a coated Ni or Co base superalloy article having resistance to oxidation and thermal fatigue.

The superalloys are a class of materials which exhibit desirable mechanical properties at high temperatures. These alloys generally contain major amounts of nickel, cobalt and/or iron either alone or in combination, as their basis material, and alloying additions of elements such as chromium, aluminum, titanium, and the refractory metals. Superalloys have found numerous applications in gas turbine engines.

In most gas turbine applications, it is important to protect the surface of the engine component from oxidation and corrosion degradation, as such attack may materially shorten the useful life of the component, and cause significant performance and safety problems.

Coatings can be used to protect superalloy engine components from oxidation and corrosion. The well known family of coatings commonly referred to as MCrAlY coatings, where M is selected from the group consisting of iron, nickel, cobalt, and various mixtures thereof, can markedly extend the service life of gas turbine engine blades, vanes, and like components. MCrAlY coatings are termed overlay coatings, denoting the fact that they are deposited onto the superalloy surface as an alloy, and do not interact significantly with the substrate during the deposition process or during service use. As is well known in the art, MCrAlY coatings can be applied by various techniques such as physical vapor deposition, sputtering or plasma spraying. MCrAlY coatings may also include additions of noble metals, hafnium, or silicon, either alone or in combination. They may also include other rare earth elements in combination with or substitution for yttrium. See, e.g., the following US-A-3,542,530, 3,918 139, 3,928,026, 3,993,454, 4,034,142 and Re. 32, 121.

US patent Re. 32 121 states that MCrAlY coatings are the most effective coatings for protecting superalloys from oxidation and corrosion attack.

Aluminide coatings are also well known in the art as capable of providing oxidation and corrosion protection to superalloys. See, for example, US-A-3,544,348, 3,961,098, 4,070,507 and 4,132,816.

During the aluminizing process there is significant interaction between the aluminum and the substrate; the substrate chemistry and deposition temperature exert a major influence on coating chemistry, thickness and properties. A disadvantage of aluminide coatings is that in the thicknesses required for optimum oxidation and corrosion resistance, generally taught by the prior art to be about 0.0889 mm (0.0035 inches), the coatings are brittle and can crack when subjected to the stresses which gas turbine engine blades and vanes typically experience during service operation. These cracks may propagate into the substrate and limit the structural life of the superalloy component; the tendency to crack also results in poor oxidation and corrosion resistance, as discussed in US-A-3,928,026, 4,246,323, 4,382,976 and Re. 31,339.

Aluminide coatings less than about 0.0889 mm (0.0035 inches) thick may have improved crack resistance, but the oxidation resistance of such thin aluminides is not as good as that of the MCrAlY coatings.

In US-A-3,873,347 and 4,080,486 an attempt is made to combine the advantages of MCrAlY coatings and aluminide coatings. Therein, an MCrAlY coating, preferably 0.076-0.127 mm (0.003-0.005 inches) thick, is aluminized in a pack cementation process, wherein radially aligned defects in the MCrAlY coating are infiltrated with aluminum diffusing inwardly from the pack mixture. More importantly, a high concentration of aluminum results at the outer surface of the MCrAlY coating, which improves the high temperature oxidation resistance of the coating as compared to the untreated MCrAlY. Both patents state that in laboratory tests, the aluminized MCrAlY coating exhibited improved corrosion resistance, although this is somewhat at variance with the conventional wisdom that aluminum enrichment improves oxidation resistance rather than corrosion resistance.

According to US patent No. Re. 30,995, in order to prevent cracking and spalling of an aluminized MCrAlY coating from the substrate, the aluminum must not diffuse into the substrate; aluminum may diffuse no closer than 0.012 mm (0.0005 inches) to the MCrAlY/substrate interface. It is also stated that the aluminum content in the aluminized MCrAlY must be less than ten weight percent, in order to achieve the best combination of coating properties.

In US-A-3,961,098, an MCr powder is flame sprayed onto a metallic substrate in such a manner that the powder particles are substantially non-molten when they strike the substrate surface. Aluminum is subsequently diffused through the overlay coating, and into the substrate surface. Laboratory tests revealed that the aluminizing step must be conducted so that the final aluminum concentration in the coating is less than 20 weight percent, or else the coating will be brittle, and will have unacceptable corrosion and oxidation resistance.

US-A-4,246,323 teaches a process for enriching an MCrAlY coating with aluminum. The processing is conducted so that Al diffuses only into the outer surface of the MCrAlY. The outer, Al rich portion of the coating is reported to be resistant to oxidation degradation, and the inner, unaluminized MCrAlY reportedly has good mechanical properties.

5 In US patent No. Re. 31,339 an MCrAlY coated superalloy component is aluminized, and then the coated component is hot isostatically pressed. A substantial increase in coating life is reported, which is attributed to the presence of a large reservoir of an aluminum rich phase in the outer portion of the MCrAlY. As in the patents discussed above, the aluminum diffuses only into the MCrAlY outer surface. US-A-4,152,223 discloses a process similar to that of US patent No. Re. 31,339, in which an MCrAlY coated
10 superalloy is surrounded by a metallic envelope, and then hot isostatically pressed to close any defects in the MCrAlY coating and to diffuse a portion of the envelope into the overlay. If aluminum foil is used as the envelope, the foil may melt during hot isostatic pressing and form intermetallic compounds with the substrate. It is stated that these compounds may enhance the oxidation resistance of the coating. However, such intermetallics may have an undesired effect on the fatigue strength of the coated component.

15 In US-A-4,382,976, an MCrAlY coated superalloy component is aluminized in a pack process wherein the pressure of the inert carrier gas is cyclicly varied. Aluminum infiltrates radially aligned defects of the overlay, and reacts with the MCrAlY to form various intermetallic, aluminum containing phases. The extent of Al diffusion into the substrate alloy was reported to be significantly less than if the aluminizing were carried out directly on the substrate.

20 In US-A-4,101,713, high energy milled MCrAlY powders are applied to superalloy substrates by flame spray techniques. It is stated that the coated component can be aluminized, whereby aluminum would diffuse into the MCrAlY coating, and if desired, into the substrate material. However, according to US patent No. Re. 30,995 (issued to the same inventor) diffusion of aluminum into the substrate may cause spalling of the MCrAlY coating from the substrate.

25 Other US patents which disclose aluminized MCrAlY coatings are 3 874 901 and 4 123 595.

In US-A-4 005 989 a superalloy component is first aluminized and then an MCrAlY overlay is deposited over the aluminized layer. The two layer coating is heat treated at elevated temperatures, but no information is given as to the results of such heat treatment. The coating was reported to have improved resistance to oxidation degradation compared to the aluminized MCrAlY coatings discussed above.

30 Other patents which indicate the general state of the art relative to coatings for superalloys include US-A- 3 676 085, 3 928 026, 3 979 273, 3 999 956, 4 109 061, 4 123 594, 4 132 816, 4 198 442, 4 248 940 and 4 371 570.

EP-A- 0 024 802 discloses a method of forming a corrosion resistant coating on a metallic article in depositing a metallic or ceramic layer on a metallic component. Aluminum or chromium is vapour deposited
35 to react with the substrate to form an oxidation resistant coating of NiAl or NiCr.

EP-A-0 267 142 discloses a method for forming an yttrium enriched diffusion aluminide coating on a nickel or cobalt base superalloy article, comprising the step of heating the article to an elevated temperature in the presence of a powder mixture consisting of an aluminum-yttrium-X alloy, a halide activator, and a filler material not reduced by yttrium at said elevated temperature wherein X is selected from the group
40 consisting of silicon, chromium, cobalt, nickel, titanium and hafnium or is an alloy or mixture thereof.

As the operating conditions for superalloy components become more severe, further improvements are required in oxidation and corrosion resistance, and resistance to thermal mechanical fatigue. As a result, engineers are continually seeking improved coating systems for superalloys. The aforementioned advances in coating technology have markedly improved resistance to oxidation degradation. However, these
45 advances have failed to address what is know viewed as the life limiting property for coated superalloys: resistance to thermal mechanical fatigue cracking.

It is an object of the present invention to provide an improved coating system for superalloys.

Yet another object of the present invention is a low cost coating system for superalloys.

Another object of the present invention is a coating system for superalloys which has improved
50 resistance to oxidation degradation, and improved resistance to thermal mechanical fatigue.

Yet another object of the present invention is a coating system for superalloys which has the oxidation resistance of MCrAlY coatings, and the resistance to thermal mechanical fatigue cracking of thin aluminide coatings.

The process according to the present invention comprises the steps of applying an MCrAlY overlay
55 coating containing no more than 15 weight percent aluminum and where M is selected from the group consisting of iron, nickel, cobalt, and various mixtures thereof onto the surface of a nickel or cobalt base superalloy article; diffusing Al into and through the MCrAlY and into the superalloy by pack cementation techniques to form an outer coating zone containing 20-35 weight percent aluminum and a diffusion zone

between the outer zone and the substrate, wherein the diffusion zone has a lesser concentration of aluminum than the outer zone and a greater concentration of aluminum than the superalloy substrate.

The coated gas turbine engine component obtained by the process of the present invention comprises a superalloy substrate having a thin yttrium enriched aluminide coating thereon. The coating has the oxidation resistance of currently used MCrAlY coatings, and thermal fatigue life which is significantly better than current MCrAlY coatings and equal to that of the best aluminide coatings.

The coating obtained by the present invention may be produced by applying a thin, nominally 0.038 mm (0.0015 inch), overlay coating to the surface of the superalloy substrate, and then subjecting the coated component to a pack aluminizing process wherein aluminium from the pack diffuses into and through the coating and into the superalloy substrate.

The resultant invention coating has a duplex microstructure, and is 0.025 to 0.10 mm (0.001 to 0.004 inches) thick; the outer zone of the duplex microstructure ranges from between 0.012 mm to 0.076 mm (0.0005 to 0.003 inches), and comprises, inter alia, 20-35 weight percent Al enriched with 0.2-2.0 weight percent Y. The high Al content in the outer zone provides optimum oxidation resistance, and the presence of Y results in improved alumina scale adherence which reduces the rate of Al depletion from the coating during service operation.

As a result, the coating has better oxidation resistance than current aluminide coatings, and comparable or better oxidation resistance than current MCrAlY coatings. The inner, or diffusion coating zone contains a lesser concentration of aluminum than the outer zone, but a greater concentration of Al than the substrate.

The diffusion zone acts to reduce the rate of crack propagation through the coating and into the substrate. As a result, specimens coated according to the present invention have improved resistance to thermal mechanical fatigue cracking relative to overlay coated specimens, and comparable resistance to thermal mechanical fatigue cracking relative to specimens coated with the most crack resistant aluminides.

According to a preferred embodiment of the invention the overlay coating is an MCrAlY coating consisting essentially of, by weight percent, 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. More preferably, it consists essentially of 30-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. Most preferably, it consists essentially of about 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni.

According to another embodiment, this invention is a superalloy component characterized by a diffusion aluminide coating which also contains small amount of yttrium, silicon and hafnium. The resultant coating has a duplex microstructure, and is 0.025 to 0.10 mm (0.001 to 0.004 inches) thick; the outer zone of the duplex microstructure ranges from between 0.012 to 0.076 mm (0.0005 to 0.003 inches), and comprises 20-35 weight percent aluminum enriched with 0.1-5.0 weight percent yttrium, 0.1-7.0 weight percent silicon and 0.1-2.0 weight percent hafnium. The high aluminum content in the outer zone provides optimum oxidation resistance, and the presence of yttrium, silicon and hafnium improve the adherence of the alumina scale which forms during high temperature use of the coated component.

The primary advantage of the coating of the present invention is that it combines the desired properties of aluminide coatings and overlay coatings to a degree never before achieved.

Another advantage of the coating of the present invention is that it is easily applied using techniques well known in the art.

The foregoing and other objects, features and advantages of the present invention will become more apparent in the light of the following detailed description of the preferred embodiments thereof as illustrated in the accompanying drawing.

Fig. 1 is a photomicrograph (750X) of an MCrAlY overlay coating useful in producing a coating according to the present invention;

Fig. 2 is a photomicrograph (750X) of the coating according to the present invention; and

Fig. 3 shows comparative oxidation and thermal mechanical fatigue behaviour of several coatings, including the coating of the present invention.

Fig. 4 shows the results of cyclic oxidation tests of several coatings, including the coating of this invention.

The article obtained by the process of the present invention is a diffused, yttrium enriched aluminide coating for superalloys. In one embodiment described below, the coating may be produced by first applying a thin MCrAlY overlay to the surface of the superalloy, and then aluminizing the MCrAlY coated component. The resultant coating microstructure is similar to the microstructure of aluminide coatings, but contains yttrium in sufficient concentrations to markedly improve the coating oxidation resistance. Unlike simple MCrAlY overlay coatings, the coating of the present invention includes a diffusion zone which is produced during the aluminizing step, which, as will be described below, results in the coated component having desirable thermal mechanical fatigue strength.

In another embodiment the coating is a modified diffusion aluminide coating which contains small but effective amounts of yttrium, silicon and hafnium. The coating is produced by first applying a thin overlay coating to the surface of the superalloy, and then aluminizing the overlay coated component. The resultant coating microstructure is similar to the microstructure of aluminide coatings, but contains yttrium, silicon and hafnium in sufficient concentrations to markedly improve the coating oxidation resistance.

The coating has particular utility in protecting superalloy gas turbine engine components from oxidation and corrosion degradation, and has desirable resistance to thermal fatigue. Blades and vanes in the turbine section of such engines are exposed to the most severe operating conditions, and as a result, the coating of the present invention will be most useful in such applications.

The coating obtained by the process of the present invention is best described with reference to Fig. 1 and 2. Fig. 1 is a photomicrograph of an MCrAlY overlay coating approximately 0.025 mm (0.001 inches) thick, applied to the surface of a nickel base superalloy. As is typical of overlay coatings, the MCrAlY forms a discrete layer on the superalloy surface; there is no observable diffusion zone between the MCrAlY and the substrate. Fig. 2 is a photomicrograph showing the microstructure of the coating of the present invention, etched with a solution of 50 ml lactic acid, 35 ml nitric acid, and 2 ml hydrofluoric acid. The coating shown in Fig. 2 was produced by aluminizing a thin MCrAlY overlay coating similar to the coating of Fig. 1.

Metallographically, it is seen that the coating of the present invention has a duplex microstructure, characterized by an outer zone and inner, diffusion zone between the outer zone and substrate. Electron microprobe microanalysis has indicated that on a typical nickel base superalloy, the outer zone nominally contains, on a weight percent basis, 20-35 Al, 0.2-2.0 Y, up to 40 Co. and 5-30 Cr, with the balance nickel. As will be described in further detail below, the final outer zone composition results from the addition of 10-25 % Al to the preexisting MCrAlY coating composition during the aluminizing process. The diffusion zone contains a lesser concentration of Al than the outer zone, and a greater concentration of Al than the substrate; it also contains elements of the substrate. The diffusion zone also may include (Ni, Co) Al intermetallic compounds, a nickel solid solution, and various Y containing compounds.

While the coating obtained by the process of the present invention may be produced by an overlay coating process followed by a diffusion process, the resultant coating microstructure is metallographically similar to that of many aluminide coatings. Since the coating also includes a significant amount of Y, the coating of the present invention is referred to as an yttrium enriched aluminide.

With the modified diffusion aluminide coating containing yttrium, silicon and hafnium the microstructure is metallurgically similar to that shown in Fig. 1 and 2. The overlay coating is an NiCoCrAlY coating which also contains silicon and hafnium applied to the surface of a nickel base superalloy. The coating has also a duplex microstructure characterized by an outer zone and an inner diffusion zone. Electron microprobe analysis has indicated that on a typical nickel base superalloy, the outer zone nominally contains on a weight basis, 20-35 Al, 0.1-5.0 Y, 0.1-7.0 Si, 0.1-2.0 Hf, 10-40 Co and 5-30 Cr, with the balance nickel. The final zone composition results from the addition of 5-30 % Al to the preexisting overlay coating composition during the aluminizing process.

Fig. 3 presents the Relative Oxidation Life as a function of Relative Thermal Mechanical Fatigue Life for seven coatings applied to a commercially used Ni base superalloy. Relative Oxidation Life is a measure of the time to cause a predetermined amount of oxidation degradation of the substrate; in tests to determine the oxidation life of the coatings, laboratory specimens were cycled between exposures at 1150°C (2100°F) for 55 minutes and 205°C (400°F) for 5 minutes. Relative Thermal Mechanical Fatigue Life is a measure of the number of cycles until the test specimen fractures in fatigue. Test specimens were subjected to a constant tensile load while being thermally cycled to induce an additional strain equal to $\alpha\Delta T$, where α is the substrate coefficient of thermal expansion, and ΔT is the temperature range over which the specimen was cycled. The test conditions were chosen to simulate the strain and temperature cycling of a blade in the turbine section of a gas turbine engine.

Referring to Fig. 3, the Plasma Sprayed NiCoCrAlY + Hf + Si overlay is representative of the coating described in US patent No. Re. 32,121. The Electron Beam NiCoCrAlY is representative of the coating described in US-A-3,928,026. The MCrAlY over Aluminide coating is representative of the coating described in US-A-4,005,989. The coating denoted "Prior Art Aluminized MCrAlY" was a 0.15 mm (0.006 inch) NiCoCrAlY coating which was aluminized using pack cementation techniques to cause diffusion of Al into the outer 0.05 mm (0.002 inches) of the overlay.

Aluminide A is representative of a diffusion coating produced by a pack cementation process similar to that described in US-A-4,132,816, but with slight modifications to enhance the thermal fatigue resistance of the coated component. The coating denoted "Invention Aluminized MCrAlY" had a microstructure similar to that shown in Fig. 2, and was produced by aluminizing a thin overlay according to the process described

below.

As is apparent from Fig. 3, the coating of the present invention exhibits resistance to oxidation degradation which is comparable to the most oxidation resistant coating which was tested. Also, the coating of the present invention exhibits resistance to thermal mechanical fatigue which is comparable to the most crack resistant coating which was tested. Thus a unique and never before achieved combination of properties is achieved by the coating of this invention.

The coating of the present invention can be produced using techniques known in the art. One method is by aluminizing an overlay coated superalloy using pack cementation techniques. As noted above, in the prior art aluminized MCrAlY coatings, the MCrAlY is generally 0.076-0.12 mm (0.003-0.005 inches) thick. Also in the prior art, the aluminizing step is usually carried out to limit the Al content to less than 20 weight percent according to US-A-3,961,098, although US-A-Re. 30,995 specifies less than 10 weight percent. In the present invention, the overlay is relatively thin: less than 0.076 mm (0.003 inches) thick and preferably between 0.012 mm (0.0005) and 0.038 mm (0.0015 inches) thick. The aluminizing process is carried out so that the resultant Al content in the outer coating zone (Fig. 2) is at least 20%. It is believed that the desirable oxidation resistance of the coating of the present invention is due to the presence of yttrium in the outer coating zone which contains such a high aluminum content. The high Al content provides good resistance to oxidation degradation, and the presence of Y results in improved alumina scale adherence, and a resultant reduced rate of Al depletion from the coating. That the coating of the present invention has improved fatigue properties (Fig.3) when the Al content is greater than 20 % is surprising, and contrary to the teachings of the prior art. See, for example, US-A-3,961,098. The favourable resistance to thermal mechanical fatigue cracking is believed due to the thinness of the coating and the interaction of the inner and outer coating zones. The combined thickness of the outer and inner zones should be 0.025 to 0.127mm (0.001 to 0.005 inches), preferably 0.05 to 0.076 mm (0.002 to 0.003 inches). If a crack forms in the outer zone, the propagation rate of the crack will be relatively low due to the thinness of the outer zone, in accordance with crack propagation theories of Griffith, discussed in e.g., F. A. Clintock and A. S. Argon, Mechanical Behaviour of Materials, Addison-Wesley, 1966, pp. 194-195. Once the crack reaches the diffusion zone, the crack surfaces will begin to oxidize, because the diffusion zone contains a lesser concentration of Al than the outer zone. As the crack oxidizes, the surfaces of the crack will become rough, and the crack tip will become blunted thereby reducing its propagation rate.

When the diffusion aluminide coating in addition to yttrium, also contains silicon and hafnium, it is believed that the desirable oxidation resistance of the coating of the present invention is not only due to the presence of yttrium but also silicon and hafnium in the outer coating zone which contains the high aluminium content. The presence of silicon and hafnium also results in improved alumina scale adherence.

As noted above, the diffusion zone contains elements of the substrate. Superalloys generally contain refractory elements such as W, Ta, Mo, and Nb for solid solution strengthening, as discussed in US-A-4,402,772. During the elevated temperature aluminizing process, these elements tend to migrate into the diffusion zone. Some refractory elements are known to decrease oxidation resistance, and due to their presence in the diffusion zone, the diffusion zone has poorer resistance to oxidation than the outer zone and the substrate. Thus, once the crack reaches the diffusion zone, oxidation of the crack surfaces proceeds at a rate which is more rapid than the rate in either the outer zone or the substrate, thereby significantly decreasing the crack propagation rate.

The MCrAlY coating can be applied by, e.g., plasma spraying, electron beam evaporation, electroplating, sputtering, or slurry deposition. Preferably, the MCrAlY coating is applied by plasma spraying powder having the following composition, on a weight percent basis: 10-40 Co, 5-30 Cr, 5-15 Al, 1-5 Y, with the balance essentially Ni. A more preferred composition range is 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni. The most preferred composition is 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni. The plasma spray operation is carried out under conditions whereby the powder particles are substantially molten when they strike the substrate surface.

After the MCrAlY coating has been applied to the surface of the superalloy component, aluminum is diffused completely through the MCrAlY coating and to a significant depth into the superalloy substrate. Preferable, the MCrAlY coated component is aluminized using pack cementation techniques. During the aluminizing process, aluminum reacts with the MCrAlY overlay coating to transform it into an yttrium enriched aluminide coating.

The overlay coating containing silicon and hafnium is applied by plasma spraying powder particles having the following composition, on a weight percent basis: 10-40 Co, 5-30 Cr, 5-15 Al, 0.1-5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni. A more preferred composition range is 20-24 Co, 12-20 Cr, 10-14 Al, 0.1-3.5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni. The most preferred composition is about 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.4 Si, 0.2 Hf, balance Ni. The combined amounts of yttrium, silicon, and hafnium which should be in the overlay

coating is between about 0.5 and 9 weight percent. A more preferred range is 0.5-6 %. Most preferably, the combined yttrium, silicon and hafnium content is about 1.2 %. The plasma spray operation is preferably a vacuum or low pressure plasma spray operation, and powder particles are substantially molten when they strike the substrate surface. See US-A-4,585 481.

After the overlay coating has been applied to the surface of the superalloy component, aluminum is diffused completely through the overlay coating and into the superalloy substrate. Preferably, the overlay coated component is aluminized using pack cementation techniques. During the aluminizing process, aluminum reacts with the overlay coating to transform the overlay into an aluminide coating enriched with oxygen active elements, i.e., enriched with yttrium, silicon and hafnium.

While pack cementation according to e.g., US-A-3,544,348 is the preferred method for diffusing aluminum into and through the overlay, aluminum may be diffused by gas phase deposition, or by, e.g., applying a layer of aluminum (or an alloy thereof) onto the surface of the overlay, and then subjecting the coated component to a heat treatment which will diffuse the aluminum layer through the overlay and into the superalloy substrate. The layer of aluminum can also be deposited by techniques such as electroplating, sputtering, flame spraying, or by slurry techniques, followed by a heat treatment.

The present invention may be better understood through reference to the following example which is meant to be illustrative rather than limiting.

Example I

NiCoCrAlY powder having a nominal particle size range of 5-44 μm (microns) and a nominal composition of, on a weight percent basis, 20 Co, 15 Cr, 11.5 Al, 2.5 Y, balance Ni, was plasma sprayed onto the surface of a single crystal Ni-base superalloy having a nominal composition of 10 Cr, 5 Co, 4 W, 1.5 Ti, 12 Ta, 5 Al, balance Ni. The NiCoCrAlY powder was sprayed using a low pressure chamber spray apparatus (Model 005) sold by the Electro Plasma Corporation. The spray apparatus included a sealed chamber in which the specimens were sprayed; the chamber was maintained with an argon atmosphere at a reduced pressure of 6650 Pa (50 millimeters Hg). The plasma spraying was conducted at 50 volts and 1,520 amperes with 85 % Ar-15 % He arc gas. At these conditions, the powder particles were substantially molten when they impacted the superalloy surface. A powder feed rate of 0.13 kg per minute (0.3 pounds per minute) was used, and the resultant MCrAlY produced was 0.025 mm (0.001 inches) thick and was similar to the coating shown in Fig. 1.

After the NiCoCrAlY coating was applied to the superalloy surface, it was glass bead peened at an intensity of 0.43-0.48 mm N (0.017-0.019 inches N), and then the component was aluminized in a pack cementation mixture which contained, on a weight percent basis, 10 Co_2Al_5 , 1 Cr, 0.5 NH_4Cl , balance Al_2O_3 . The aluminizing process was carried out at 1025 °C (1,875 °F) for 3 hours, in an argon atmosphere. The coated component was then given a diffusion heat treatment at 1080 °C (1,975 °F) for 4 hours and a precipitation heat treatment at 870 °C (1,600 °F) for 32 hours.

Metallographic examination of the aluminized NiCoCrAlY coated Ni-base superalloy revealed a duplex microstructure, similar to that shown in Fig. 2; the outer zone was 0.05 mm (0.002 inches) thick, and the diffusion zone was 0.025 mm (0.001 inches) thick. Thus, the combined coating thickness (outer zone plus diffusion zone) was 0.076mm (0.003 inches) thick, and was 200 % greater than the initial MCrAlY coating thickness. Additionally, the diffusion zone extended inward of the outer zone an amount equal to 50% of the outer zone thickness. Preferably, the diffusion zone thickness is at least 30 % of the thickness of the outer zone. The nominal composition of the outer zone was determined by electron microprobe microanalysis, which revealed that, on a weight percent basis, the Al concentration was 24-31, the Y concentration was 0.3-0.7, the Cr concentration was 5-18, the Co concentration was less than 30, with the balance essentially Ni. The diffusion zone contained a lesser Al concentration than the outer zone, and a greater Al concentration than the substrate. In general, the Al concentration in the diffusion zone decreased as a function of depth, although the desirable properties of the coating of the present invention is not dependent on such a depth dependent Al gradient in the diffusion zone. The diffusion zone also contained compounds of the substrate elements.

In oxidation testing conducted at 1150 °C (2,100 °F), the above described coating protected the substrate from degradation for about 1,250 hours, which was comparable to the protection provided by a plasma sprayed NiCoCrAlY + Hf + Si overlay. In thermal mechanical fatigue testing, wherein specimens were subjected to a strain rate of 0.5 % while being alternately heated to a temperature of 427 °C (800 °) and 1038 °C (1,900 °F), coated nickel base single crystal superalloy test specimens had a life to failure of about 15,000 cycles, which was comparable to the life of a thin aluminide coated specimen (Aluminide B of Fig. 2).

Example II

Tests were conducted to determine whether there was a critical range of MCrAlY compositions which exhibited superior oxidation resistance when aluminized. In these tests, the MCrAlY coatings were applied by low pressure plasma spray techniques, and then peened, aluminized, and heat treated in the manner set forth in Example I. The as-applied MCrAlY coating thickness was 0.025 (0.001 inches). The MCrAlY composition evaluated in this example were as follows:

Sample	Composition (weight percent)				
	Ni	Co	Cr	Al	Y
A	47	23	18	12	0.0
B	80	0	5	6	9.1
C	0	70	15	12.5	2.5
D	44	23	18	13	1.7
E*	55	10	18	13	3.5
F	43	23	19	13	2.5
G	35	35	15	13	3.1
H	37	35	15	11	2.1

* Also contained 0.7 % Hf

Results of burner rig oxidation testing, where the specimens were heated to 1150°C (2,100°F) and held for 55 minutes, and then force air cooled for 5 minutes, are shown in Fig. 4. This figure shows that maximum oxidation resistance was achieved with compositions having a yttrium level between 2 and 3.5 percent, and a cobalt level between 20 and 38 percent. Chromium was between 12-20 percent, aluminum between 10-14 percent, and the balance was nickel. The need for particular yttrium and cobalt levels are seen on review of the data for samples F, G, and H, which had the best cyclic oxidation life of any of the samples which were tested. The oxidation resistance of the other specimens, which had yttrium and cobalt levels outside of the aforementioned range, were notably inferior, which may be at least partially explained in the following manner: the complete absence of yttrium in sample A resulted in a coating which had poor oxide scale adherence. Yttrium is noted for its beneficial effects on oxide scaled adherence, and the performance of sample A was not unexpected. The very high yttrium level in sample B resulted in a coating having an undesirably low melting point. It also resulted in a coating containing particles enriched in yttrium, which act as sites for internal oxidation (yttrium is readily oxidized). Overlay coatings characterized by the presence of such particles have poor overall oxidation resistance. Sample B also contained no cobalt and too little chromium and aluminum. Sample C shows the effect of no nickel and very high cobalt in the MCrAlY coating, even though yttrium is in the target range. Sample D shows the effect of a low yttrium content even though cobalt is in the target range. And sample E shows the effect of low cobalt even though yttrium is in the target range.

Example III

Cyclic oxidation tests were conducted at 2,100°F to compare the coating life (the number of hours required to oxidize one mil of coating) of an overlay coating having the NiCoCrAlY composition preferred in the practice of this invention with the invention yttrium enriched aluminide coating made with the same NiCoCrAlY composition. The nominal composition of the NiCoCrAlY was Ni-35Co-15Cr-11Al-2.5Y, and the overlay coating was sprayed, peened and then heat treated in the manner set forth in Example I. The yttrium enriched aluminide coating was also made in the manner set forth in Example I.

These tests indicated that the coating life of the overlay coating was 170 hours per 25.4 μm (mil), while the life of the invention coating was 410 hours per 25.4 μm (mil). The invention process improved the coating life nearly 150 %.

Example IV

Powder having a nominal particle size range of 5-44 μm (microns) and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.4 Si, 0.2 Hf, balance nickel, was plasma sprayed onto the surface of a nickel base superalloy having a nominal composition of 10 Cr, 5 Co, 4 W, 1.5 Ti, 12 Ta, 5

Al, balance nickel. The powder was sprayed using a low pressure chamber spray apparatus (Model 005) sold by the Electro Plasma Corporation. The spray apparatus included a sealed chamber in which the specimens were sprayed; the chamber was maintained with an argon atmosphere at a reduced pressure of 6650 Pa (50 millimeters Hg). The plasma spraying was conducted at about 50 Volts and 1,520 Amperes with 85 % Ar-15 % He arc gas. At these conditions, the powder particles were substantially molten when they impacted the superalloy surface. A powder feed rate of 0.13 kg (0.3 pounds) per minute was used, and the resultant overlay produced was 0.025 mm (0.001 inches) thick and was similar to the coating shown in Fig. 1.

After the overlay coating was applied to the superalloy surface, it was glass bead peened at an intensity of 0.43-0.48 mm N (0.017-0.019 inches N), and then the component was aluminized in a pack cementation mixture which contained, on a weight percent basis, 10 Co₂Al₅, 1 Cr, 0.5 NH₄Cl, balance Al₂O₃. The aluminizing process was carried out at 1025 °C (1,875 °F) for 3 hours, in an argon atmosphere. The coated component was then given a diffusion heat treatment at 1080 °C (1,975 °F) for 4 hours and a precipitation heat treatment at 870 °C (1,600 °F) for 32 hours.

Metallographic examination of the aluminized overlay coated nickel base superalloy component revealed a duplex microstructure, similar to that shown in Figure 2; the outer zone was 0.05 mm (0.002 inches) thick, and the diffusion zone was about 0.025 mm (0.001 inches) thick. Thus, the combined coating thickness (outer zone plus diffusion zone) was 0.076 mm (0.003 inches) thick, and was 200 % greater than the initial overlay coating thickness. Additionally, the diffusion zone extended inward of the outer zone an amount equal to 50 % of the outer zone thickness. Preferably, the diffusion zone thickness is at least 30 % of the thickness of the outer zone. The nominal composition of the outer zone was determined by electron microprobe microanalysis, which revealed that, on a weight percent basis, the aluminum concentration was about 24-31, the yttrium concentration was 0.2-0.3, the hafnium concentration was 0.05-0.15, the silicon concentration was 0.1-0.2, the chromium concentration was 5-18, the cobalt concentration was less than 30, with the balance essentially nickel. The diffusion zone contained a lesser aluminum concentration than the outer zone, and a greater aluminum concentration than the substrate. In general, the aluminum concentration in the diffusion zone decreased as a function of depth, although the desirable properties of the coating of the present invention is not dependent on such an aluminum gradient in the diffusion zone. The diffusion zone also contained compounds of the substrate elements.

In oxidation testing conducted at 1150 °C (2,100 °F) the invention coating protected the substrate from degradation for about 1,250 hours, which was at least equivalent to the protection provided by a plasma sprayed NiCoCrAlY + Hf + Si overlay. In thermal mechanical fatigue testing, wherein specimens were subjected to a strain rate of 0.5 % while being alternately heated to a temperature of 427 °C (800 °F) and 1038 °C (1,900 °F), coated nickel base single crystal superalloy test specimens had a life to failure of about 15,000 cycles, which was at least comparable to the life of a thin aluminide coated specimen (Aluminide B of Fig. 2).

Example V

Powder having a nominal size range of 5-44 μm (microns) and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.3 Si, 0.2 Hf balance nickel was plasma sprayed onto the nickel base superalloy described in Example I using the same parameters described in Example I.

The coating was then glass bead peened and aluminized as described in Example I. Oxidation testing at 1150 °C (2,100 °F) showed the coating to be protective of the substrate for a period of time of about 1,250 hours.

Example VI

Powder having a nominal particle size of about 5-44 μm (microns) and a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.5 Y, 2.2 Si was plasma sprayed onto the nickel base superalloy described in Example I, using the parameters described in Example I. The coating was also peened and aluminized as described in Example I. In oxidation testing at 1150 °C (2,100 °F), the coating protected the substrate for 900 hours.

Example VII

Powder having a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.3 Y, 0.5 Si, 0.6 Ce was sprayed, peened and aluminized as described in Example I. In oxidation tests at 1150 °C

(2,100°F), the coating protected the substrate for a period of time of about 750 hours.

Example VIII

5 Powder having a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.3 Y, 1.2 Hf was sprayed, peened and aluminized as described in Example I. In oxidation testing at 1150°C (2,100°F), the coating protected the substrate for a period of time of 650 hours.

Example IX

10 Oxidation testing of a simple aluminide coating applied in the manner generally described by Boone et al. in US-A-3,544,348 was oxidation tested at 1150°C (2,100°F). The aluminide coating protected the substrate from oxidation for a period of time of 375 hours.

Thus, the coatings described in the aforementioned Examples, all being aluminized overlay coatings, 15 had significantly greater resistance to oxidation than the simple aluminide coating of Example IX.

Even though the Examples discussed above show that yttrium or the combination of yttrium, silicon and hafnium are preferred elements in the overlay coating, other elements which have similar oxygen active properties can be used. These elements include cerium, and the other rare earth elements, as those elements are known to those skilled in the art. At least two of such oxygen active elements should be 20 present in the overlay coating, in an amount which ranges between 0.5 and 9 weight percent.

Claims

1. A process for producing a coated nickel or cobalt base superalloy article having resistance to oxidation 25 and thermal fatigue, comprising the steps of applying an MCrAlY overlay coating containing no more than 15 weight percent aluminum onto the superalloy surface and where M is selected from the group consisting of iron, nickel, cobalt, and various mixtures thereof; diffusing aluminum into and through the MCrAlY and into the superalloy by pack cementation techniques to form an outer coating zone containing 20-35 weight percent aluminum, and a diffusion zone between the outer zone and the 30 superalloy substrate, wherein the diffusion zone has a lesser concentration of aluminum than the outer zone and a greater concentration of aluminum than the superalloy substrate.
2. The process of claim 1, wherein the MCrAlY overlay is applied to a thickness of between 0.0127-0.076 mm (0.0005 and 0.003 inches).
3. The process of claim 1, wherein the MCrAlY overlay is applied to a thickness of between 0.0127-0.038 35 mm (0.0005 and 0.0015 inches).
4. The process of claim 1, wherein the combined thickness of the outer zone and diffusion zone is at least 100 % greater than the initial MCrAlY overlay coating thickness.
5. The process of claim 1, wherein the MCrAlY overlay is applied by plasma spraying powder in such a manner that the powder particles are substantially molten when they strike the superalloy surface.
6. The process of claim 5, wherein said plasma spray powder contains at least 5 weight percent 45 aluminum.
7. The process of claim 1, wherein the overlay coating on the article surface is a NiCoCrAlY coating which consists of, by weight percent, 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y balance Ni and the combined 50 thickness of the outer zone and diffusion zone is 0.025-0.10 mm (0.001-0.004 inches).
8. The process of claim 7, wherein the NiCoCrAlY coating consists of 30-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni.
9. The process of claim 7, wherein the NiCoCrAlY coating consists of 35 Co, 15 Cr, 11 Al, 2.5 Y, balance 55 Ni.



(2,100 °F), the coating protected the substrate for a period of time of about 750 hours.

Example VIII

- 5 Powder having a nominal composition of, on a weight percent basis, 22 Co, 17 Cr, 12.5 Al, 0.3 Y, 1.2 Hf was sprayed, peened and aluminized as described in Example I. In oxidation testing at 1150 °C (2,100 °F), the coating protected the substrate for a period of time of 650 hours.

Example IX

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Oxidation testing of a simple aluminide coating applied in the manner generally described by Boone et al. in US-A-3,544,348 was oxidation tested at 1150 °C (2,100 °F). The aluminide coating protected the substrate from oxidation for a period of time of 375 hours.

- 15 Thus, the coatings described in the aforementioned Examples, all being aluminized overlay coatings, had significantly greater resistance to oxidation than the simple aluminide coating of Example IX.

Even though the Examples discussed above show that yttrium or the combination of yttrium, silicon and hafnium are preferred elements in the overlay coating, other elements which have similar oxygen active properties can be used. These elements include cerium, and the other rare earth elements, as those elements are known to those skilled in the art. At least two of such oxygen active elements should be
20 present in the overlay coating, in an amount which ranges between 0.5 and 9 weight percent.

Claims

- 25 1. A process for producing a coated nickel or cobalt base superalloy article having resistance to oxidation and thermal fatigue, comprising the steps of applying an MCrAlY overlay coating containing no more than 15 weight percent aluminum onto the superalloy surface and where M is selected from the group consisting of iron, nickel, cobalt, and various mixtures thereof; diffusing aluminum into and through the MCrAlY and into the superalloy by pack cementation techniques to form an outer coating zone
30 containing 20-35 weight percent aluminum, and a diffusion zone between the outer zone and the superalloy substrate, wherein the diffusion zone has a lesser concentration of aluminum than the outer zone and a greater concentration of aluminum than the superalloy substrate.
2. The process of claim 1, wherein the MCrAlY overlay is applied to a thickness of between 0.0127-0.076 mm (0.0005 and 0.003 inches).
- 35 3. The process of claim 1, wherein the MCrAlY overlay is applied to a thickness of between 0.0127-0.038 mm (0.0005 and 0.0015 inches).
4. The process of claim 1, wherein the combined thickness of the outer zone and diffusion zone is at least
40 100 % greater than the initial MCrAlY overlay coating thickness.
5. The process of claim 1, wherein the MCrAlY overlay is applied by plasma spraying powder in such a manner that the powder particles are substantially molten when they strike the superalloy surface.
- 45 6. The process of claim 5, wherein said plasma spray powder contains at least 5 weight percent aluminum.
7. The process of claim 1, wherein the overlay coating on the article surface is a NiCoCrAlY coating which consists of, by weight percent, 20-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y balance Ni and the combined
50 thickness of the outer zone and diffusion zone is 0.025-0.10 mm (0.001-0.004 inches).
8. The process of claim 7, wherein the NiCoCrAlY coating consists of 30-38 Co, 12-20 Cr, 10-14 Al, 2-3.5 Y, balance Ni.
- 55 9. The process of claim 7, wherein the NiCoCrAlY coating consists of 35 Co, 15 Cr, 11 Al, 2.5 Y, balance Ni.



10. The process of claim 1 wherein said overlay coating contains yttrium, silicon and hafnium, and the combined thickness of the outer coating zone and the diffusion zone is 0.025-0.127mm (0.001-0.005 inches).
- 5 11. The process of claim 10, wherein the overlay coating is applied to a thickness of between 0.0127-0.038 mm (0.0005 and 0.0015 inches).
12. The process of claim 10, wherein the combined thickness of the outer zone and diffusion zone is at least 100 % greater than the initial overlay coating thickness.
- 10 13. The process of claim 10, wherein the overlay coating is applied by plasma spraying powder in such a manner that the powder particles are substantially molten when they strike the superalloy surface.
14. The process of claim 10, wherein said plasma spray powder contains at least 5 weight percent aluminum.
- 15 15. The process of claim 10, wherein the coating thickness is 0.050-0.076 mm (0.002-0.003 inches).
16. The process of claim 10, wherein the combined thickness of the coating is 0.050-0.076 mm (0.002-0.003 inches).
- 20 17. The process of claim 10, wherein the overlay coating is applied by a low pressure plasma spray process.
18. The process of claim 10, wherein the overlay coating is peened before the step of diffusing.
- 25 19. The process of claim 10, wherein the overlay coating consists of, by weight percent, 10-40 Co, 5-30 Cr, 5-15 Al, 0.1-5 Y, 0.1-7 Si, 0.1-2 Hf, balance Ni.
- 30 20. The process of claim 19, wherein the overlay coating consists of, by weight percent, 22 Co, 17 Cr, 12.5 Al, 0.6 Y, 0.4 Si, 0.2 Hf, balance Ni.
21. The process of claim 19, wherein the combined amount of yttrium, silicon and hafnium in the overlay coating is between 0.5 and 9 percent.
- 35 22. The process of claim 19, wherein the combined amount of yttrium, silicon and hafnium in the overlay coating is between 1 and 2 percent.
23. The process of claim 10, wherein said coating contains at least two oxygen active elements selected from the group comprising yttrium, silicon, hafnium, cerium and other rare earth elements in a combined amount between 0.5 and 9 weight percent and the combined thickness of the outer coating zone and the diffusion zone is 0.025-0.127 mm (0.001-0.005 inches).
- 40 24. An article having resistance to oxidation and thermal mechanical fatigue obtainable by the process according to claims 1-23.
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Patentansprüche

1. Verfahren zum Herstellen eines überzogenen Nickel- oder Kobaltsuperlegierungsgegenstands, der eine Beständigkeit gegen Oxidation und Wärmeermüdung hat, beinhaltend die Schritte Auftragen eines MCrAlY-Overlay-Überzugs, der nicht mehr als 15 Gewichtsprozent Aluminium enthält, auf die Superlegierungs-oberfläche, wobei M aus der Gruppe ausgewählt wird, die aus Eisen, Nickel, Kobalt und verschiedenen Gemischen derselben besteht; Diffundieren von Aluminium in und durch das MCrAlY und in die Superlegierung durch Pulverzementierungstechniken, um eine äußere Überzugszone zu bilden, die 20-35 Gewichtsprozent Aluminium enthält, und eine Diffusionszone zwischen der äußeren Zone und dem Superlegierungs-substrat, wobei die Diffusionszone eine geringere Konzentration an Aluminium als die äußere Zone und eine größere Konzentration an Aluminium als das Superlegierungs-substrat hat.
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2. Verfahren nach Anspruch 1, wobei der MCrAlY-Overlay-Überzug bis zu einer Dicke zwischen 0,0127-0,076 mm (0.0005 und 0.003 Zoll) aufgetragen wird.
- 5 3. Verfahren nach Anspruch 1, wobei der MCrAlY-Overlay-Überzug bis zu einer Dicke zwischen 0,0127-0,038 mm (0.0005 und 0.0015 Zoll) aufgetragen wird.
4. Verfahren nach Anspruch 1, wobei die kombinierte Dicke der äußeren Zone und der Diffusionszone wenigstens 100 % größer als die anfängliche MCrAlY-Overlay-Überzugsdicke ist.
- 10 5. Verfahren nach Anspruch 1, wobei der MCrAlY-Overlay-Überzug durch Plasmaspritzen von Pulver derart aufgebracht wird, daß die Pulverpartikeln im wesentlichen schmelzflüssig sind, wenn sie auf die Superlegierungsoberfläche auftreffen.
- 15 6. Verfahren nach Anspruch 5, wobei das Plasmaspritzpulver wenigstens 5 Gewichtsprozent Aluminium enthält.
- 20 7. Verfahren nach Anspruch 1, wobei der Overlay-Überzug auf der Gegenstandsoberfläche ein NiCoCrAlY-Überzug ist, der, in Gewichtsprozent, aus 20-38 Co, 12-20 Cr, 10-14 Al, 2-3,5 Y, Rest Ni, besteht und wobei die kombinierte Dicke der äußeren Zone und der Diffusionszone 0,025-0,10 mm (0.001-0.004 Zoll) beträgt.
- 25 8. Verfahren nach Anspruch 7, wobei der NiCoCrAlY-Überzug aus 30-38 Co, 12-20 Cr, 10-14 Al, 2-3,5 Y, Rest Ni, besteht.
- 30 9. Verfahren nach Anspruch 7, wobei der NiCoCrAlY-Überzug aus 35 Co, 15 Cr, 11 Al, 2,5 Y, Rest Ni, besteht.
10. Verfahren nach Anspruch 1, wobei der Overlay-Überzug Yttrium, Silicium und Hafnium enthält und wobei die kombinierte Dicke des äußeren Überzugs und der Diffusionszone 0,025-0,127 mm (0.001-0.005 Zoll) beträgt.
- 35 12. Verfahren nach Anspruch 10, wobei die kombinierte Dicke der äußeren Zone und der Diffusionszone wenigstens 100 % größer ist als die anfängliche Overlay-Überzugsdicke.
- 40 13. Verfahren nach Anspruch 10, wobei der Overlay-Überzug durch Plasmaspritzen eines Pulvers derart aufgetragen wird, daß die Pulverpartikeln im wesentlichen schmelzflüssig sind, wenn sie auf die Superlegierungsoberfläche auftreffen.
14. Verfahren nach Anspruch 10, wobei das Plasmaspritzpulver wenigstens 5 Gewichtsprozent Aluminium enthält.
- 45 15. Verfahren nach Anspruch 10, wobei die Überzugsdicke 0,050-0,076 mm (0.002-0.003 Zoll) beträgt.
16. Verfahren nach Anspruch 10, wobei die kombinierte Dicke des Überzugs 0,050-0,076 mm (0.002-0.003 Zoll) beträgt.
- 50 17. Verfahren nach Anspruch 10, wobei der Overlay-Überzug durch einen Niederdruckplasmaspritzprozeß aufgetragen wird.
18. Verfahren nach Anspruch 10, wobei der Overlay-Überzug vor dem Schritt des Diffundierens gehämmert wird.
- 55 19. Verfahren nach Anspruch 10, wobei der Overlay-Überzug, in Gewichtsprozent, aus 10-40 Co, 5-30 Cr, 5-15 Al, 0,1-5 Y, 0,1-7 Si, 0,1-2 Hf, Rest Ni, besteht.



20. Verfahren nach Anspruch 19, wobei der Overlay-Überzug, in Gewichtsprozent, aus 22 Co, 17 Cr, 12,5 Al, 0,6 Y, 0,4 Si, 0,2 Hf, Rest Ni, besteht.
- 5 21. Verfahren nach Anspruch 19, wobei die kombinierte Menge an Yttrium, Silicium und Hafnium in dem Overlay-Überzug zwischen 0,5 und 9 Prozent beträgt.
22. Verfahren nach Anspruch 19, wobei die kombinierte Menge an Yttrium, Silicium und Hafnium in dem Overlay-Überzug zwischen 1 und 2 Prozent liegt.
- 10 23. Verfahren nach Anspruch 10, wobei der Überzug wenigstens zwei sauerstoffaktive Elemente, die aus der Gruppe ausgewählt werden, welche Yttrium, Silicium, Hafnium, Cer und andere seltene Erdelemente umfaßt, in einer kombinierten Menge zwischen 0,5 und 9 Gewichtsprozent enthält und die kombinierte Dicke der äußeren Überzugszone und der Diffusionszone 0,025-0,127 mm (0.001-0.005 Zoll) beträgt.
- 15 24. Gegenstand mit einer Beständigkeit gegen Oxidation und thermomechanische Ermüdung, der durch das Verfahren nach den Ansprüchen 1-23 erzielbar ist.

Revendications

- 20 1. Un procédé pour la production d'un article en superalliage à base de nickel ou de cobalt enduit, résistant à l'oxydation et à la fatigue thermique, comprenant les étapes de l'application d'un enduit de recouvrement MCrAlY, ne contenant pas plus de 15 % en poids d'aluminium, sur la surface du superalliage, et dans lequel M est sélectionné dans le groupe consistant en fer, nickel, cobalt et divers mélanges de ceux-ci; la diffusion de l'aluminium dans et à travers le MCrAlY et dans le superalliage par
25 des techniques de cémentation en masse, pour former une zone d'enduit externe, contenant 20-35 % en poids d'aluminium et une zone de diffusion, entre la zone externe et le substrat en superalliage, dans lequel la zone de diffusion a une concentration plus faible en aluminium que la zone externe et une concentration en aluminium plus importante que le substrat en superalliage.
- 30 2. Le procédé de la revendication 1, dans lequel le revêtement MCrAlY est appliqué avec une épaisseur comprise entre 0,0127-0,076 mm (0,0005 et 0,003 pouce).
3. Le procédé de la revendication 1, dans lequel le revêtement MCrAlY est appliqué avec une épaisseur comprise entre 0,0127-0,038 mm (0,0005 et 0,0015 pouce).
- 35 4. Le procédé de la revendication 1, dans lequel l'épaisseur combinée de la zone externe et de la zone de diffusion est au moins 100 % supérieure à l'épaisseur initiale de l'enduit de recouvrement MCrAlY.
5. Le procédé de la revendication 1, dans lequel le revêtement MCrAlY est appliqué par pulvérisation au plasma d'une poudre, d'une telle manière que les particules de poudre sont essentiellement fondues quand elles heurtent la surface du superalliage.
- 40 6. Le procédé de la revendication 5, dans lequel ladite poudre pulvérisée au plasma contient au moins 5 % en poids d'aluminium.
- 45 7. Le procédé de la revendication 1, dans lequel l'enduit de recouvrement, sur la surface de l'article, est un enduit NiCoCrAlY qui consiste, en pourcentage en poids, en 20-38 Co, 12-20 Cr, 10-14 Al, 2-3,5 Y, le complément étant du Ni et l'épaisseur combinée de la zone externe et de la zone de diffusion est de 0,025-0,10 mm (0,001-0,004 pouce).
- 50 8. Le procédé de la revendication 7, dans lequel l'enduit NiCoCrAlY consiste en 30-38 Co, 12-20 Cr, 10-14 Al, 2-3,5Y, le complément étant Ni.
9. Le procédé de la revendication 7, dans lequel l'enduit NiCoCrAlY consiste en 35 Co, 15 Cr, 11 Al, 2,5 Y, le complément étant Ni.
- 55 10. Le procédé de la revendication 1, dans lequel ledit enduit de recouvrement contient de l'yttrium, du silicium et de l'hafnium et, l'épaisseur combinée de la zone de l'enduit externe et de la zone de



diffusion est de 0,025-0,127 mm (0,001-0,005 pouce).

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11. Le procédé de la revendication 10, dans lequel l'enduit de recouvrement est appliqué avec une épaisseur comprise entre 0,0127-0,038 mm (0,0005 et 0,0015 pouce).
12. Le procédé de la revendication 10, dans lequel l'épaisseur combinée de la zone externe et de la zone diffusion est au moins 100 % supérieure à l'épaisseur de l'enduit de recouvrement initiale.
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13. Le procédé de la revendication 10, dans lequel l'enduit de recouvrement est appliqué par pulvérisation au plasma d'une poudre, d'une telle manière que les particules de poudre sont essentiellement fondues quand elles heurtent la surface du superalliage.
14. Le procédé de la revendication 10, dans lequel ladite poudre pulvérisée au plasma contient au moins 5 % en poids d'aluminium.
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15. Le procédé de la revendication 10, dans lequel l'épaisseur de l'enduit est de 0,050-0,076 mm (0,002-0,003 pouce).
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16. Le procédé de la revendication 10, dans lequel l'épaisseur combinée de l'enduit est de 0,050-0,076 mm (0,002-0,003 pouce).
17. Le procédé de la revendication 10, dans lequel l'enduit de recouvrement est appliqué par un procédé de pulvérisation au plasma à basse pression.
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18. Le procédé de la revendication 10, dans lequel l'enduit de recouvrement est martelé avant l'étape de diffusion.
19. Le procédé de la revendication 10, dans lequel l'enduit de recouvrement consiste, en pourcentage en poids, en 10-40 Co, 5-30 Cr, 5-15 Al, 0,1-5 Y, 0,1-7 Si, 0,1-2 Hf, le complément étant du Ni.
- 30
20. Le procédé de la revendication 19, dans lequel l'enduit de recouvrement consiste, en pourcentage en poids, en 22 Co, 17 Cr, 12,5 Al, 0,6 Y, 0,4 Si, 0,2 Hf, le complément étant du Ni.
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21. Le procédé de la revendication 19, dans lequel la quantité combinée d'yttrium, de silicium et d'hafnium, dans l'enduit de recouvrement est comprise entre 0,5 et 9 pourcents.
22. Le procédé de la revendication 19, dans lequel la quantité combinée d'yttrium, de silicium et d'hafnium, dans l'enduit de recouvrement est comprise entre 1 et 2 pourcents.
- 40
23. Le procédé de la revendication 10, dans lequel ledit enduit contient au moins deux éléments actifs, en présence d'oxygène, sélectionnés dans le groupe contenant l'yttrium, le silicium, l'hafnium, le cérium et d'autres métaux des terres rares, en une quantité combinée comprise entre 0,5 et 9 pourcents en poids et l'épaisseur combinée de la zone de l'enduit externe et de la zone de diffusion est de 0,025-0,127 mm (0,001-0,005 pouce).
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24. Un article ayant une résistance à l'oxydation et à la fatigue mécanique thermique, que l'on peut obtenir par le procédé selon les revendications 1-23.
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