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(54) **High temperature corrosion resistant composite coatings**

Hochtemperatur-korrosionsbeständige zusammengesetzte Beschichtungen

Revêtements composites résistant à la corrosion à haute température

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Description

The present invention relates to so-called "MCrAlY" overlay coating systems modified to enhance resistance of superalloy gas turbine components to high temperature oxidation and corrosion attack.

The term "MCrAlY" is a shorthand way of referring to well known temperature and oxidation/corrosion resistant alloy systems comprising in general one or more of nickel, cobalt and iron as the major "M" constituent, together with chromium and aluminium in quite large amounts, plus (usually) a minor amount of yttrium or other rare earth element. In weight percentage terms, such alloys may be broadly defined as having the following compositions:

Cr - 10 to 50%
Al - 4 to 30%
Y - 0 to 3%
Fe/Co/Ni - balance.

For example, one well known alloy, used as the basis of the present work, has a nominal composition in weight percent of:

Cr - 25%
Al - 12%
Y - 0.5%
Co - balance

As mentioned above, these alloys are frequently used as protective coatings for superalloy components exposed to high temperatures in corrosive environments. In tests, we have found that the above CoCrAlY alloy, in the form of an overlay coating applied by an argon shrouded plasma spraying technique, has given satisfactory high temperature protection and mechanical properties for nickel based superalloys such as IN738. This superalloy is available from the International Nickel company, and has the nominal composition in weight percent of:

Cr-16%, Al-3.4%, Ti-3.4%, Co-8.5%, W-2.6%,
Mo-1.75%, Ta-1.75%, Cb-0.9%, Fe-0.5%, Si-0.3%,
Mn-0.2%, C-0.17%, Zr-0.1%, B-0.01%, Ni-Balance.

One problem with all protective coatings of this type, particularly in highly corrosive marine environments, is gradual degradation in service due to continued mobility of elements within the coatings and from the base material at the high operating temperatures of the turbines of gas turbine engines. Elements such as Mo,W,Ti,Ta, and Cr present within a superalloy such as IN738 migrate into the coating, thus reducing the basic mechanical properties of the superalloy. Furthermore, elements at the surface of the coatings, such as Al,Cr,Co,Ni,Ti, etc., are consumed during service by oxidation and sulphidation and therefore have to be replaced continuously to afford continued protection. Such replacement occurs by means of migration to the surface from the bulk of the coating and ultimately from the superalloy base material.

It is already known to improve the ability of MCrAlY protective coatings to resist high temperature oxidation and corrosion by aluminising them to produce an aluminide layer on top of the MCrAlY coating. In this context, "high temperature" means above about 750 °C. For example, British patent GB 1457033 discloses nickel- or cobalt - based superalloy components coated as follows:

a) vapour deposited MCrAlY coating;
b) further vapour deposited coating of aluminium on top of the MCrAlY coating;
c) heat treatment of the duplex coated component to cause the inter-diffusion of the aluminium and the MCrAlY coatings.

Such coatings have been further improved upon by incorporating further refractory oxidation/corrosion resistant metallic elements such as platinum and hafnium into the outer aluminium coating and then diffusion heat treating the resulting duplex coating to produce an aluminide layer containing the refractory elements. For example, patent no. US 4123594 discloses Fe,Co, and Ni based superalloy components which are coated as follows:

a) vapour deposited MCrAl(Y)-type first coating;
b) application of further coating containing aluminium and at least one of the elements Hf and Pt - specifically, Al-Hf coatings were applied by a pack coating process and an alternative Al-Hf-Pt coating was applied by sputtering of Pt onto the first coating, followed by application of an Al-Hf coating by a pack coating process;
c) heat treatment of the coated component to cause the inter-diffusion of the coatings, so producing a graded coating in which the outer portion consists of 10-30% Al and 2-5%Hf, with, in the case of the Pt-containing coating, 20-40%Pt.

This patent also mentions rhenium and paladium as possible constituents of the outer portions of the coatings as additions to, or substitutions for, platinum and hafnium.

The contents of the above prior patent specifications should be consulted for further and more complete details of the compositions and processes summarised above.

It should be noted that, at least to some extent, MCrAlY coatings do act as a barrier between the base material and any outer aluminide coating to limit migration of base material elements, particularly aluminium and chromium, during service.

We prefer to apply MCrAlY coatings by the argon shrouded plasma spray process as mentioned above, proprietary to Union Carbide Coatings Service Corpora-

tion, of Indianapolis, U.S.A. After spraying, the coatings can be aluminised, but must, of course, be heat treated to inter-diffuse them with the base material.

As a result of aluminising an existing MCrAlY coating, stable aluminides of the "M" constituent(s) of the MCrAlY coating are produced in the top layer of the resulting coating, such as nickel and/or cobalt aluminides, resulting in improved hot oxidation/corrosion resistance. In service, some of the Al component in the aluminides gradually migrates to the surface of the coating, where it is converted to alumina (Al_2O_3), so producing a corrosion/oxidation resistant barrier. Nevertheless, this barrier is gradually eroded and is replaced by further oxidation of aluminium migrating from the aluminides below.

Ideally, the required extra Al to maintain the concentration of aluminides in the surface layers of the coating could be supplied from the MCrAlY inner portion of the coating. But in the case of MCrAlY alloys with aluminium concentrations near the lower end of the above-mentioned ranges (say, 4 to 20 wt.%, e.g., 12%, as in the specific example mentioned above), the Al content is insufficient for the migration mechanism to be able to continue to supply the deficient surface layers with Al for a lengthy period. Despite this, MCrAlY coatings with such relatively low aluminium contents are preferred because higher Al contents tend to make the coating brittle in service after the necessary diffusion heat treatment has been carried out.

Consequently, it is desired to improve the hot corrosion and oxidation performance of aluminised plasma-sprayed MCrAlY coatings in which the MCrAlY component of the coating has a relatively low Al content of 4 to 20wt.% in the as-applied condition.

In addition to the hot oxidation/corrosion resistance referred to above, it is also desirable to improve the ability of MCrAlY coatings to resist low temperature oxidation and corrosion, "low temperature" in the present context meaning about 550 - 750 °C. This, of course, should be accomplished without any detrimental effect on the high temperature protection afforded by the coatings.

One known way of improving low temperature oxidation/ corrosion resistance of any coating system is to increase the concentration of chromium, at least near the surface layer of the coating. Generally speaking, it has been found that low temperature oxidation/ corrosion resistance improves as Cr concentration levels in the coating increase to about 40%, but that further increases above 40% are deleterious. The process of increasing the Cr content of an existing coating is called chromising, and is usually accomplished by known vapour or pack chromising methods, such as those marketed by Chromalloy Corporation.

Chromising improves low temperature oxidation/ corrosion resistance of coating systems because Cr oxidises to form chromia, Cr_2O_3, which forms a protective oxide film at the coating surface. Unfortunately, chromising is ineffective to improve high temperature oxidation/corrosion resistance of coating systems. This is because Cr_2O_3 dissociates into Cr and gaseous CrO_3 at temperatures above about 750°C.

Accordingly, the present invention includes a process for providing an M-based superalloy base material, where M is at least one of iron, cobalt and nickel, with a graded multiplex protective coating system containing aluminides in and near its surface, the process comprising the steps of:

applying an alloy coating material of the MCrAlY type to the surface of the base material, the Al content of the coating material being in the range 4 to 20 wt.%;

optionally, chromising the MCrAlY-type coating to produce a coating with a chromised top layer having extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the MCrAlY-type coating after chromising being not more than about 40%, preferably 35 to 40%;

aluminising the coating resulting from the preceding utilised process step to produce a coating having a surface layer containing aluminides of the M constituent of the coating;

depositing a platinum layer onto the surface of the aluminised coating, and

heat treating the resulting coating to diffuse the platinum layer into the underlying aluminide containing layer, thereby to produce an MCrAlY coating having a platinum modified aluminide surface layer.

Preferably, the platinum layer has a thickness of 5 to 15μm when applied, and the subsequent diffusing heat treatment is conveniently that normally utilised to restore the properties of the base material after the aluminising step. In the case of alloy IN738, this is one hour diffusion treatment at 1120°C, gas fan quench, and age 24 hours at 845°C.

Given the above heat treatment time, the thickness of the platinum layer as deposited is very important to the final structure of the above coating. Utilising a deposited platinum layer having a thickness of 10 to 15μm gives a structure comprising an MCrAlY coating having a single surface layer containing platinum modified aluminide. This is achieved because during heat treatment the platinum and the underlying aluminides inter-diffuse completely.

Alternatively, to obtain a structure comprising an MCrAlY coating having a double surface layer in the form of a top layer containing platinum modified aluminide and a sub-surface layer containing aluminides substantially without platinum modification, the deposited platinum layer should have a thickness of 5 to 10μm. This can be achieved because during heat treatment the platinum and the underlying aluminides do not inter-diffuse completely.

The present invention also includes an alternative process for providing an M-based superalloy base ma-

terial, where M is at least one of iron, cobalt and nickel, with a graded multiplex protective coating system containing aluminides with enhanced aluminium content in and near its surface, the process comprising the steps of:

applying an alloy coating material of the MCrAlY type to the surface of the base material, the Al content of the coating material being in the range 4 to 20 wt.%;

optionally, chromising the MCrAlY-type coating to produce a coating with a chromised top layer having extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the MCrAlY-type coating after chromising being not more than about 40%, preferably 35 to 40%;

depositing a platinum layer onto the surface of the coating resulting from the preceding utilised process step,

heat treating the resulting coating to diffuse the platinum layer into the underlying MCrAlY coating, and aluminising the coating resulting from the preceding step and heat treating to diffuse the aluminium into the surface of the platinised coating, thereby to produce an MCrAlY coating having a surface layer containing platinum modified aluminides of the M constituent of the coating.

Preferably, the platinum layer has a thickness of 5 to 10μm when applied.

The time of aluminising is very important to the final structure of the above coating. Utilising a deposited platinum layer of the above thickness, to obtain a structure comprising an MCrAlY coating having a single surface layer containing platinum modified aluminide, the platinised coating should be aluminised only for a relatively short time of about 4 to 6 hours at the aluminising temperature. This will allow the aluminium to diffuse into the platinised coating only about as far as the platinum has already diffused. Alternatively, to obtain a structure comprising an MCrAlY coating having a double surface layer in the form of a top layer containing platinum modified aluminide and a sub-surface layer containing aluminides substantially without platinum modification, the platinised coating should be aluminised for a relatively long time of about 6 to 12 hours at the aluminising temperature. This will allow the aluminium to diffuse into the platinised coating further than the platinum has already diffused.

The chromising step in the above processes, if performed, is performed essentially to obtain a large gradient of concentration of Cr in and near the surface of the MCrAlY coating. This increases its low temperature sulphidation resistance.

An increase in the chromium content of various superalloy coating systems increases their low temperature sulphidation resistance, though an upper limit of about 40wt.% Cr content is usually adhered to because too high a Cr content causes excessive brittleness. This low temperature sulphidation resistance is achieved because Cr in the coating oxidises to chromia (Cr_2O_3), which is a relatively inert at temperatures below about 750°C. However, above 750°C, chromia dissociates, with the escape from the surface of the coating of CrO_3 gas and consequent disruption of the oxide surface scale, leaving the underlying layer open to further corrosive attack. Hence, Cr enrichment of MCrAlY coatings is conventionally understood to be ineffective to increase sulphidation resistance at temperatures above about 750°C.

However, in our invention, we have found that by enriching the Cr content of the MCrAlY coating, preferably up to its maximum advisable limit of about 40wt.% utilising the chromising step, and thereafter aluminising, optionally platinising (alternatively, and preferably, this optional platinising step can be done before aluminising, which has the effect of increasing the concentration of Al in the resulting layer of platinum modified aluminide), and finally heat treating, we produce a synergistic effect in which the presence of high concentrations of aluminides along with the high concentrations of chromium in the surface layer(s) of the MCrAlY coating changes the reaction kinetics of the chromia at the surface of the coating at temperatures above about 750°C, such that dissociation of chromia encourages the formation of further alumina, which is resistant to corrosive attack at these temperatures.

Examples of various prior art coatings and coatings according to the invention will now be described with reference to the accompanying figures, in which:

Figure 1 is a diagrammatic micrograph section indicating the general characteristics of a known aluminised MCrAlY coating;

Figures 2 and 3 are diagrammatic micrograph sections indicating the general characteristics of two variant coatings according to the present invention;

Figure 4 is a graph showing the effect of sulphidation corrosion on various tested coatings;

Figure 5 is a photomicrograph of a section of a preferred coating according to the invention, seen at a magnification of 200X; and

Figure 6 is a graphical representation of the results of a microprobe analysis of a coating similar to that shown in Figure 5.

In tests of the effectiveness of various modifications to the CoCrAlY overlay coating system described above, the overlay coating was first applied to IN738 alloy bars by the previously mentioned argon shrouded plasma spray technique. Extra elements were then introduced into the outer layer of the coating using various methods as described below:

(1) Vapour aluminise at 1090°C for six hours, then heat treat to restore the properties of the base mate-

rial, i.e. one to two hours diffusion treatment at 1120°C, gas fan quench, and age 24 hours at 845°C. A diagrammatic representation of the resulting structure is shown in Figure 1.

(2) Vapour aluminise as in (1), clean by controlled blasting procedure, then platinum plate the coating to a thickness of 15μm, then heat treat as in (1) to inter-diffuse the MCrAlY coating with the Pt layer and restore the properties of the base material. The resulting structure is diagrammatically shown in Figure 2. .

(3) Vapour aluminise as in (1), clean by controlled blasting procedure, then platinum plate the coating to a thickness of 8μm, then heat treat as in (1) to inter-diffuse the MCrAlY coating with the Pt layer and restore the properties of the base material. The resulting structure is diagrammatically shown in Figure 3.

(4) Vapour chromise at 1100°C for five hours in a sealed retort, then additionally process as (2). The resulting structure is as for Figure 2, except that the aluminide layer is enriched by Cr.

(5) Vapour chromise at 1100°C for five hours in a sealed retort, then additionally process as (3). Resulting structure as for Figure 3, except that the aluminide layers are enriched by Cr.

(6) Vapour chromise at 1100°C for five hours in a sealed retort, then additionally process as (1). Resulting structure as for Figure 1, except that the aluminide layer is enriched by Cr.

In addition to the above six processes involving modification of an initial MCrAlY coating, two further coating systems were tried:

(7) Process as (5), but without an initial MCrAlY base coat.

(8) MCrAlY base coat only.

The major coating processes referred to above are characterised as follows.

The vapour aluminising process took place in an argon-filled retort vessel, with the parts to be aluminised being suspended in close proximity over packs of aluminising powder which liberate aluminium halide gas when heated. Aluminium from the gas is deposited onto the parts and diffuses into it due to the elevated temperature. A commercial example of this technique is the RT69 (trade name) process available from Chromalloy U.K. Limited, of Bramble Way, Clover Nook Industrial Estate, Somercoates, Derby DE55 4RH, England, or its parent company, Chromalloy Research and Technology, Blaisdell, Orangeburg, NY 10962, U.S.A.

Platinum plating was accomplished by an electroplating process, again available from Chromalloy at the sites mentioned above under the trade name RT22.

Vapour chromising is performed in a similar way to vapour aluminising and is also available from Chromalloy under the trade name CN70.

The samples processed as outlined above were subjected to simulated isothermal sulphidation tests. The coated test pieces were placed in a Nimonic boat and covered with 50/50 mixture of Na_2SiO_3 and MoS_2 paste. The samples were then tested at 850°C in a muffle furnace for times of up to 3550 hours. At intervals a sample of each coating system type was removed and carefully prepared for microscopic examination. The depth of attack was recorded for each test piece. Results of this test are given in Figure 4, which is a graph of depth of penetration of the coating in μm (microns) against time of the test in hours.

Below is a short commentary on the microscopic examinations of the tested samples for each type of coating mentioned in paragraphs 1 to 8 above.

(1) An Al rich outer layer had been produced in the outer part of the MCrAlY coating. Sulphidation attack was observed mainly in the Al rich outer layer, with no attack within the MCrAlY.

(2) A platinum modified aluminide layer ($PtAl_2$ + CoAl) had been produced in the outer part of the MCrAlY coating. However, the Al concentration in wt.% within this layer was found to be poor, affording inferior protection against sulphidation attack compared with (1).

(3) A platinum modified aluminide layer ($PtAl_2$ + CoAl) had been produced in the outer part of the MCrAlY coating, on top of a cobalt aluminide layer (CoAl). Increased Al concentration in the platinum modified aluminide layer afforded better protection than (2).

(4) A chromium enriched platinum modified aluminide layer ($PtAl_2$ + CoAl) had been produced in the outer part of the MCrAlY coating, on top of a chromium enriched MCrAlY coating layer. However, the Al concentration in wt.% within the platinum modified alumina layer was found to be poor, showing only marginally greater protection against sulphidation attack compared with (1).

(5) A chromium enriched platinum modified aluminide layer ($PtAl_2$ + CoAl) had been produced in the outer part of the MCrAlY coating, on top of a chromium enriched cobalt aluminide layer (CoAl). Increased Al concentration in the platinum modified aluminide layer afforded better protection than (4).

(6) A chromium enriched aluminide outer layer had been produced in the outer part of the chromised MCrAlY coating. Sulphidation attack was greater than for (1) due to Al concentration not being sufficiently high, but the presence of additional chromium throughout would improve oxidation protection at lower temperatures.

(7) A chromium enriched aluminide surface layer had been produced on the superalloy specimen. This showed very poor protection against sulphidation, partly due to low Al concentration.

(8) The plain MCrAlY coating exhibited much inferior protection to the aluminised MCrAlY layer of (1), but was better than (7).

As can be seen from Figure 4, overall best performance in the sulphidation tests was given by coating (5), which had been chromised, aluminised and platinised with the 8μm (micron) platinum plate diffused layer.

Next best performers were coatings (4), (6), (3) and (2), which were very close together in apparent sulphidation performance. Coating (4) had been processed in the same way as coating (5), except for the application of the thicker 16μm (micron) platinum plate. Coating (6) had been chromised and aluminised, but not platinised. Coatings (3) and (2) had been aluminised and platinised, but not chromised.

The trend shown here is that sulphidation performance is increased by the chromising step, and increased even further by platinising, provided that aluminium concentrations in the platinum modified aluminide layer can be kept as high as possible. Lower concentrations of aluminium in such cases are associated with application of thicker platinum plate for diffusion.

Figure 5 shows a typical microstructure of coating (5) at x200 magnification before sulphidation testing, with the various layers indicated. Figure 6 shows the result of an electron probe microanalysis of this coating, in which the concentration in weight percentage terms of various elements in the coating is graphically plotted against the depth of the coating in μm (microns). Here it can be seen that the Cr content of the coating is up to about 40wt.% in the chromised layer, up to about 20 wt.% in the platinum aluminide layer and about 25wt.% retained in the body of the MCrAlY coating. On the other hand, the highest aluminium content is only about 20 wt.% and is less than this near the surface of the coating in the platinum modified layer. It should be noted that the results of the electron probe microanalysis as plotted are subject to variation due to experimental error and to local variations in element concentrations in the small scale microstructure.

From the work as detailed above it was evident that with samples (4) and (5) the Al concentration in the outer zones was lower than is generally accepted to be optimum in aluminide coatings. Consequently, further work was undertaken with test pieces in which the process activity and sequence of operation were altered to increase the Al concentration level to 25 - 30%. Alterations were essentially to apply the platinum plate directly onto the chromised MCrAlY overlay coating and platinise by diffusion heat treating at 1050°C for 2 hours before the aluminising step. Depending upon the depth of the platinum plate as applied and the time for which the platinised coating was subsequently aluminised (thicker platinum modified layers require longer aluminising times), it was found that the structures illustrated in Figures 5 and 6 could be reproduced, but with increased Al concentrations of 25-30% in the aluminide layers. This increased Al concentration enabled achievement of the required synergistic effect of extra alumina scale production at the surface of the coating at high temperatures consequent upon dissociation of chromia, thereby enhancing high temperature sulphidation resistance.

Although of maximum advantage when utilised in conjunction with the chromising step, the method of platinising an MCrAlY coating before aluminising it, in order to gain higher Al concentrations in the platinum modified aluminide surface layer of the finished coating, will also plainly be advantageous when utilised without the prior chromising step.

Although the above description has concentrated on the use of a CoCrAlY overlay coating on an IN738 nickel based superalloy substrate, the invention is plainly more generally applicable to MCrAlY-type coatings on a variety of superalloy substrates.

Claims

1. A process for providing an M-based superalloy base material, where M is at least one of iron, cobalt and nickel, with a graded multiplex protective coating system containing aluminides in and near its surface, the process including the steps of:

   applying an alloy coating material of the MCrAlY type to the surface of the base material, the Al content of the coating material being in the range 4 to 20 wt.%; and
   aluminising the coating to produce a coating having a surface layer containing aluminides of the M constituent of the coating;
   the process being characterised by the following additional process steps:
   after the application of the MCrAlY type coating and before the aluminising step, optionally chromising the MCrAlY-type coating to produce a coating with a chromised top layer having extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the MCrAlY-type coating after chromising being not more than about 40%;

after the aluminising step, depositing a platinum layer onto the surface of the aluminised coating, and

heat treating the resulting coating to platinise it by diffusing the platinum layer into the underlying aluminide containing layer, thereby to produce an MCrAlY coating having a platinum modified aluminide surface layer.

2. A process according to claim 1, in which the thickness of the platinum as applied and the subsequent heat treatment are such that during heat treatment the platinum and the underlying aluminides inter-diffuse completely to give a coating structure comprising an MCrAlY coating having a single surface layer containing platinum modified aluminide.

3. A process according to claim 2, in which the platinum layer has a thickness of 10 to 15μm when applied.

4. A process according to claim 1, in which the thickness of the platinum as applied and the subsequent heat treatment are such that during heat treatment the platinum and the underlying aluminides do not inter-diffuse completely, thereby giving a coating structure comprising an MCrAlY coating having a double surface layer in the form of a top layer containing platinum modified aluminide and a sub-surface layer containing aluminides substantially without platinum modification.

5. A process according to claim 4, in which the platinum layer has a thickness of 5 to 10μm when applied.

6. A process according to any one of claims 1 to 5, in which the platinum diffusing heat treatment is that normally utilised to restore the properties of the base material after the aluminising step.

7. A process for providing an M-based superalloy base material, where M is at least one of iron, cobalt and nickel, with a graded multiplex protective coating system containing aluminides with enhanced aluminium content in and near its surface, the process including the steps of:

applying an alloy coating material of the MCrAlY type to the surface of the base material, the Al content of the coating material being in the range 4 to 20 wt.%; and

aluminising the coating to produce a coating having a surface layer containing aluminides of the M constituent of the coating;

the process being characterised by the following additional process steps performed after application of the MCrAlY type coating material and before aluminising:

optionally, chromising the MCrAlY-type coating to produce a coating with a chromised top layer having extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the MCrAlY-type coating after chromising being not more than about 40%;

depositing a platinum layer onto the surface of the coating resulting from the preceding utilised process step, and

heat treating the resulting coating to platinise it by diffusing the platinum layer into the underlying MCrAlY coating to produce an MCrAlY coating having a surface layer containing platinum modified aluminides of the M constituent of the coating, whereby when the platinised coating is aluminised the aluminium is diffused into the surface of the platinised coating.

8. A process according to claim 1 or claim 7, the total chromium content in the surface layer of the MCrAlY-type coating after chromising being in the range 35 to 40%.

9. A process according to claim 1 or claim 7, in which the platinum layer has a thickness of 5 to 15μm when applied.

10. A process according to claim 7, in which the thickness of the platinum as applied, the platinising heat treatment and the subsequent aluminising step are such that during aluminising the aluminium diffuses into the platinised coating only about as far as the platinum has already diffused, thereby giving a coating structure comprising an MCrAlY coating having a single surface layer containing platinum modified aluminide.

11. A process according to claim 7, in which the thickness of the platinum as applied, the platinising heat treatment and the subsequent aluminising step are such that during aluminising the aluminium diffuses into the platinised coating further than the platinum has already diffused, thereby giving a coating structure comprising an MCrAlY coating having a double surface layer in the form of a top layer containing platinum modified aluminide and a sub-surface layer containing aluminides substantially without platinum modification.

12. A process according to claim 10, in which the platinum layer has a thickness of 5 to 10μm when applied and the aluminising step comprises vapour aluminising at 1090°C for about four to six hours.

13. A process according to claim 11, in which the platinum layer has a thickness of 5 to 10μm when applied and the aluminising step comprises vapour aluminising at 1090°C for about six to twelve hours.

14. A process according to any preceding claim, in which the platinising heat treatment comprises heating at 1050°C for two hours.

15. A coated article comprising an M-based superalloy base material and a multiplex protective MCrAlY coating system, where M is at least one of iron, cobalt and nickel, the coating having a surface layer containing aluminides of platinum and the M constituent of the coating,
characterised in that the surface layer contains extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the coating being not more than about 40%.

16. A coated article comprising an M-based superalloy base material and a multiplex protective MCrAlY coating system, where M is at least one of iron, cobalt and nickel, the coating having a surface layer containing aluminides of platinum and the M constituent of the coating,
characterised in that the surface layer is a double surface layer in the form of a top layer containing platinum modified aluminide and a sub-surface layer containing aluminides substantially without platinum modification.

17. A coated article according to claim 16, in which the surface layer has extra chromium in solid solution in the M constituent of the coating, the total chromium content in the surface layer of the coating being not more than about 40%.

18. A coated article according to claim 15 or claim 17, in which the total chromium content in the surface layer of the coating is in the range 35 to 40%.

Patentansprüche

1. Verfahren zur Erzeugung eines Superlegierungs-Basismaterials auf M-Basis, wobei M wenigstens eines der Elemente Eisen, Kobalt und Nickel ist, mit einem gestuften Multiplexschutzüberzugssystem, welches Aluminide in seiner Oberfläche und in der Nähe der Oberfläche enthält, wobei das Verfahren die folgenden Schritte umfaßt:

- es wird ein Legierungsüberzugsmaterial der MCrAlY-Type auf die Oberfläche des Basismaterials aufgebracht, wobei der Al-Gehalt des Überzugsmaterials im Bereich zwischen 4 und 20 Gew.-% liegt; und

- es wird der Überzug aluminisiert, um einen Überzug zu erhalten, dessen Oberflächenschicht Aluminide der M-Komponenten des Überzugs enthält,

wobei das Verfahren durch die folgenden zusätzlichen Schritte gekennzeichnet ist:

- nach der Aufbringung des MCrAlY-Überzugs und vor der Aluminisierungsstufe erfolgt fakultativ eine Chromisierung des MCrAlY-Überzugs, um einen Überzug mit einer chromisierten Deckschicht zu erhalten, die weiteres Chrom in fester Lösung in der M-Komponente des Überzugs enthält, wobei der Gesamtchromgehalt in der Oberflächenschicht des MCrAlY-Überzugs nach der Chromisierung nicht mehr als etwa 40 % beträgt;

- nach der Aluminisierungsstufe wird eine Platinschicht auf der Oberfläche des aluminisierten Überzugs abgelagert, und

- es wird der resultierende Überzug einer Wärmebehandlung unterworfen, um ihn durch Diffusion der Platinschicht in die darunterliegende Aluminide enthaltende Schicht zu platinisieren, wodurch ein MCrAlY-Überzug geschaffen wird, der eine durch Platin modifizierte Aluminidoberflächenschicht aufweist.

2. Verfahren nach Anspruch 1, bei welchem die Dicke des aufgebrachten Platins und die folgende Wärmebehandlung derart sind, daß während der Wärmebehandlung das Platin und die darunterliegenden Aluminide vollständig zusammendiffundieren, um einen Überzugsaufbau zu schaffen, der aus einem MCrAlY-Überzug besteht, welcher eine einzige Oberflächenschicht besitzt, die durch Platin modifiziertes Aluminid aufweist.

3. Verfahren nach Anspruch 2, bei welchem die Platinschicht eine Dicke zwischen 10 und 15 µm aufweist, wenn sie aufgebracht wird.

4. Verfahren nach Anspruch 1, bei welchem die Dicke der aufgebrachten Platinschicht und die folgende Wärmebehandlung derart sind, daß während der Wärmebehandlung Platin und die darunterliegenden Aluminide nicht vollständig miteinander diffundieren, wodurch ein Überzugsaufbau geschaffen wird, der einen MCrAlY-Überzug mit einer Doppeloberflächenschicht aufweist, die aus einer Deckschicht mit durch Platin modifiertem Aluminid und einer darunterliegenden Schicht besteht, die Aluminide im wesentlichen ohne Platinmodifikation enthält.

5. Verfahren nach Anspruch 4, bei welchem die Platinschicht eine Dicke zwischen 5 bis 10 µm aufweist, wenn sie aufgebracht wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, bei

welchem die Platindiffusionswärmebehandlung jene ist, die normalerweise benutzt wird, um die Eigenschaften des Basismaterials nach der Aluminisierungsstufe wiederherzustellen.

7. Verfahren zur Erzeugung eines Superlegierungs-Basismaterials der M-Basis, wobei M wenigstens eines der Elemente Eisen, Kobalt und Nickel ist, mit einem gestuften Multiplexschutzüberzugssystem, welches Aluminide mit erhöhtem Aluminiumgehalt in der Oberfläche oder in der Nähe hiervon aufweist, wobei das Verfahren die folgenden Schritte aufweist:

- es wird ein Legierungsüberzugsmaterial der MCrAlY-Type auf die Oberfläche des Basismaterials aufgebracht, wobei der Al-Gehalt des Überzugsmaterials im Bereich zwischen 4 bis 20 Gew.-% liegt; und

- es wird der Überzug aluminisiert, um einen Überzug zu erzeugen, der eine Oberflächenschicht besitzt, die Aluminide der M-Komponente des Überzugs enthält;

wobei das Verfahren durch die folgenden zusätzlichen Verfahrensschritte gekennzeichnet ist, die nach Aufbringung des Überzugsmaterials der MCrAlY-Type und vor der Aluminisierung durchgeführt werden:

- es wird fakultativ der MCrAlY-Überzug chromisiert, um einen Überzug mit einer chromisierten Deckschicht zu erzeugen, die gesondert Chrom in fester Lösung in der M-Komponente des Überzugs besitzt, wobei der Gesamtchromgehalt der Oberflächenschicht des MCrAlY-Überzugs nach der Chromisierung nicht mehr als ungefähr 40 % beträgt;

- es wird eine Platinschicht auf der Oberfläche des Überzugs abgelagert, die durch den vorhergehenden Verfahrensschritt hergestellt wurde, und

- es erfolgt eine Wärmebehandlung des resultierenden Überzugs, um diesen durch Diffusion der Platinschicht in den darunterliegenden MCrAlY-Überzug zu platinisieren und einen MCrAlY-Überzug zu erzeugen, der eine Oberflächenschicht besitzt, die durch Platin modifizierte Aluminide der M-Komponente des Überzugs enthält, wodurch bei Aluminisierung des platinisierten Überzugs das Aluminium in die Oberfläche des platinisierten Überzugs diffundiert.

8. Verfahren nach den Ansprüchen 1 oder 7, bei welchem der Gesamtchromgehalt in der Oberflächenschicht des MCrAlY-Überzugs nach der Chromisierung in dem Bereich zwischen 35 und 40 % liegt.

9. Verfahren nach den Ansprüchen 1 oder 7, bei welchem die Platinschicht bei Aufbringung eine Dicke von 5 bis 15 µm besitzt.

10. Verfahren nach Anspruch 7, bei welchem die Dicke der Platinschicht beim Aufbringen, die Platinisierungswärmebehandlung und der folgende Aluminisierungsschritt derart durchgeführt werden, daß während der Aluminisierung das Aluminium in den platinisierten Überzug nur etwa so weit diffundiert, wie das Platin bereits diffundiert ist, wodurch ein Überzugsaufbau geschaffen wird, der einen MCrAlY-Überzug aufweist, welcher eine einzige Oberflächenschicht besitzt, die durch Platin modifiziertes Aluminid aufweist.

11. Verfahren nach Anspruch 7, bei welchem die Dicke der Platinschicht bei ihrer Aufbringung, die Platinisierungswärmebehandlung und der darauffolgende Aluminisierungsschritt derart sind, daß während der Aluminisierung das Aluminium in den platinisierten Überzug hinein weiter diffundiert als das Platin bereits diffundiert ist, wodurch ein Oberflächenaufbau geschaffen wird, der aus einem MCrAlY-Überzug in Gestalt einer Doppeloberflächenschicht besteht, die ihrerseits aus einer Deckschicht, welche durch Platin modifiziertes Aluminid enthält, und einer unter der Oberfläche liegenden Schicht besteht, die Aluminide im wesentlichen ohne Platinmodifikation enthält.

12. Verfahren nach Anspruch 10, bei welchem die Platinschicht eine Dicke zwischen 5 und 10 µm aufweist, wenn sie aufgebracht wird, und der Aluminisierungsschritt eine Dampfaluminisierung bei 1090 °C während vier bis sechs Stunden umfaßt.

13. Verfahren nach Anspruch 11, bei welchem die Platinschicht eine Dicke zwischen 5 und 10 µm aufweist, wenn sie aufgebracht wird, und der Aluminisierungsschritt eine Dampfaluminisierung bei 1090 °C während etwa sechs bis zwölf Stunden umfaßt.

14. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die Platinisierungswärmebehandlung eine Erhitzung bei 1050 °C während zwei Stunden umfaßt.

15. Mit Überzug versehenes Werkstück, bestehend aus einem Superlegierungs-Basismaterial auf M-Basis und einem Multiplexschutz-MCrAlY-Überzugssystem, wobei M wenigstens eines der Elemente Eisen, Kobalt und Nickel ist und der Überzug eine Oberflächenschicht besitzt, die Aluminide von Platin

und M-Komponenten des Überzugs aufweist, dadurch gekennzeichnet, daß die Oberflächenschicht zusätzlich Chrom in fester Lösung in der M-Komponente des Überzugs enthält, wobei der Gesamtchromgehalt in der Oberflächenschicht des Überzugs nicht mehr als 40 % beträgt.

16. Mit Überzug versehenes Werkstück, bestehend aus einem Superlegierungs-Basismaterial auf M-Basis und einem Multiplexschutz-MCrAlY-Überzugssystem, wobei M wenigstens eines der Elemente Eisen, Kobalt und Nickel ist und der Überzug eine Oberflächenschicht besitzt, die Aluminide von Platin und M-Komponenten des Überzugs aufweist, dadurch gekennzeichnet, daß die Oberflächenschicht eine Doppeloberflächenschicht ist, die aus einer Deckschicht, welche durch Platin modifiziertes Aluminid enthält, und einer unter der Oberfläche liegenden Schicht besteht, die Aluminide im wesentlichen ohne Platinmodifikation enthält.

17. Mit Überzug versehenes Werkstück nach Anspruch 16, bei welchem die Oberflächenschicht gesondert Chrom in fester Lösung in der M-Komponente des Überzugs enthält, wobei der Gesamtchromgehalt in der Oberflächenschicht des Überzugs nicht mehr als etwa 40 % beträgt.

18. Mit Überzug versehenes Werkstück nach den Ansprüchen 15 oder 17, bei dem der Gesamtchromgehalt in der Oberflächenschicht des Überzugs in dem Bereich zwischen 35 und 40 % liegt.

Revendications

1. Procédé pour fournir à un matériau de base de superalliage à base de M, où M est au moins un parmi le fer, le cobalt et le nickel, un système de revêtement de protection multiple stratifié comprenant des aluminures dans et à proximité de sa surface, le procédé comprenant les étapes de :

appliquer un matériau de revêtement en alliage du type MCrAlY à la surface du matériau de base, la teneur en aluminium du matériau de revêtement étant de d'ordre de 4 à 20% en poids; et
aluminer le revêtement pour produire un revêtement ayant une couche de surface contenant des aluminures du constituant M du revêtement ;

le procédé étant caractérisé par les étapes de procédé additionnelles suivantes :

après application du revêtement du type MCrAlY et avant l'étape d'aluminisation, chromiser optionnellement le revêtement du type MCrAlY pour produire un revêtement avec une couche supérieure chromisée ayant du chrome ajouté en solution solide dans le constituant M du revêtement, la teneur totale en chrome dans la couche de surface du revêtement du type MCrAlY après chromisation n'étant pas supérieure à environ 40% ;
après l'étape d'aluminisation, déposer une couche de platine sur la surface du revêtement aluminé, et
traiter thermiquement le revêtement résultant pour le platiner par diffusion de la couche de platine dans la couche sous-jacente contenant l'aluminure, pour produire ainsi un revêtement de MCrAlY ayant une couche de surface d'aluminure modifiée au platine.

2. Procédé selon la revendication 1, dans lequel l'épaisseur du platine tel qu'appliqué et le traitement thermique ultérieur sont tels que pendant le traitement thermique, le platine et les aluminures sous-jacentes interdiffusent complètement pour donner une structure de revêtement comprenant un revêtement de MCrAlY ayant une seule couche de surface contenant de l'aluminure modifiée au platine.

3. Procédé selon la revendication 2, dans lequel la couche de platine a une épaisseur de 10 à 15 µm lorsqu'appliquée.

4. Procédé selon la revendication 1, dans lequel l'épaisseur du platine tel qu'appliqué et le traitement thermique ultérieur sont tels que pendant le traitement thermique le platine et les aluminures sous-jacentes n'interdiffusent pas complètement donnant ainsi une structure de revêtement comprenant un revêtement de MCrAlY ayant une couche de surface double sous la forme d'une couche supérieure contenant de l'aluminure modifiée au platine et une couche de sous-surface contenant des aluminures essentiellement sans modification au platine.

5. Procédé selon la revendication 4, dans lequel la couche de platine a une épaisseur de 5 à 10 µm lorsqu'appliquée.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le traitement thermique de diffusion du platine est celui normalement utilisé pour restaurer les propriétés du matériau de base après l'étape d'aluminisation.

7. Procédé pour fournir à un matériau de base de superalliage à base de M, où M est au moins un parmi le fer, le cobalt et le nickel, un système de revêtement

de protection multiple stratifié contenant des aluminures avec une teneur en aluminium augmentée dans et à proximité de sa surface, le procédé comprenant les étapes de :

appliquer un matériau de revêtement en alliage du type MCrAlY à la surface du matériau de base, la teneur en aluminium du matériau de revêtement étant de d'ordre de 4 à 20% en poids ; et
aluminer le revêtement pour produire un revêtement ayant une couche de surface contenant des aluminures du constituant M du revêtement ; le procédé étant caractérisé par les étapes de procédé additionnelles suivantes :
effectuer après application du matériau de revêtement du type MCrAlY et avant aluminisation :
chromiser optionnellement le revêtement du type MCrAlY pour produire un revêtement avec une couche supérieure chromisée ayant du chrome ajouté en solution solide dans le constituant M du revêtement, la teneur totale en chrome dans la couche de surface du revêtement du type MCrAlY après chromisation n'étant pas supérieure à environ 40%;
déposer une couche de platine sur la surface du revêtement résultant de l'étape de procédé précédente utilisée, et
traiter thermiquement le revêtement résultant pour le platiner par diffusion de la couche de platine dans la couche de MCrAlY sous-jacente pour produire un revêtement de MCrAlY ayant une couche de surface contenant des aluminures modifiées au platine du constituant M du revêtement, où, lorsque le revêtement platiné est aluminé, l'aluminium est diffusé dans la surface du revêtement platiné.

8. Procédé selon la revendication 1 ou la revendication 7, dans lequel la teneur totale en chrome dans la couche de surface du revêtement du type MCrAlY après chromisation est de l'ordre de 35 à 40%.

9. Procédé selon la revendication 1 ou la revendication 7, dans lequel la couche de platine à une épaisseur de 5 à 15 µm lorsqu'appliquée.

10. Procédé selon la revendication 7, dans lequel l'épaisseur du platine lorsqu'appliqué, le traitement thermique de platinage et l'étape d'aluminisation ultérieure sont tels que pendant l'aluminisation, l'aluminium diffuse dans le revêtement platiné seulement environ aussi loin que le platine a déjà diffusé donnant ainsi une structure de revêtement comprenant un revêtement de MCrAlY ayant une seule couche de surface contenant de l'aluminure modifiée au platine.

11. Procédé selon la revendication 7, dans lequel l'épaisseur du platine lorsqu' appliqué, le traitement thermique de platinage et l'étape ultérieure d'aluminisation sont tels que pendant l'aluminisation, l'aluminium diffuse dans la couche platinée plus loin que le platine a déjà diffusé donnant ainsi une structure de revêtement comprenant un revêtement de MCrAlY ayant une couche de surface double sous la forme d'une couche supérieure contenant de l'aluminure modifiée au platine et une couche de sous-surface contenant des aluminures sensiblement sans modification au platine.

12. Procédé selon la revendication 10, dans lequel la couche de platine a une épaisseur de 5 à 10 µm lorsqu'appliquée et l'étape d'aluminisation comprend une aluminisation sous vide à 1 090°C pendant environ 4 à 6 heures.

13. Procédé selon la revendication 11, dans lequel la couche de platine à une épaisseur de 5 à 10 µm lorsqu'appliquée et l'étape d'aluminisation comprend une aluminisation sous vide à 1 090°C pendant 6 à 12 heures environ.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel le traitement thermique de platinage comprend un chauffage à 1050°C pendant deux heures.

15. Objet revêtu comprenant un revêtement de base de superalliage à base M et un système de revêtement au MCrAlY de protection multiple, où M est au moins un parmi le fer, le cobalt et le nickel, le revêtement ayant une couche de surface contenant des aluminures de platine et du constituant M du revêtement, caractérisé en ce que la couche de surface comprend du chrome ajouté en solution solide dans le constituant M du revêtement, la teneur totale en chrome dans la couche de surface du revêtement n'étant pas supérieure à environ 40%.

16. Objet revêtu comprenant un matériau de base de superalliage à base de M et un système de revêtement au MCrAlY de protection multiple, où M est au moins un parmi le fer, le cobalt et le nickel, le revêtement ayant une couche de surface contenant des aluminures de platine et du constituant M du revêtement, caractérisé en ce que la couche de surface est une couche de surface double sous la forme d'une couche supérieure contenant de l'aluminium modifié au platine et une couche de sous-surface contenant des aluminures essentiellement sans modification au platine.

17. Objet revêtu selon la revendication 16, dans lequel la couche de surface a du chrome ajouté en solution solide dans le constituant M du revêtement, la

teneur totale en chrome dans la couche de surface du revêtement n'étant pas supérieure à environ 40%.

18. Objet revêtu selon la revendication 15 ou la revendication 17, dans lequel la teneur totale en chrome dans la couche de surface du revêtement est de l'ordre de 35 à 40%.

Fig.1.

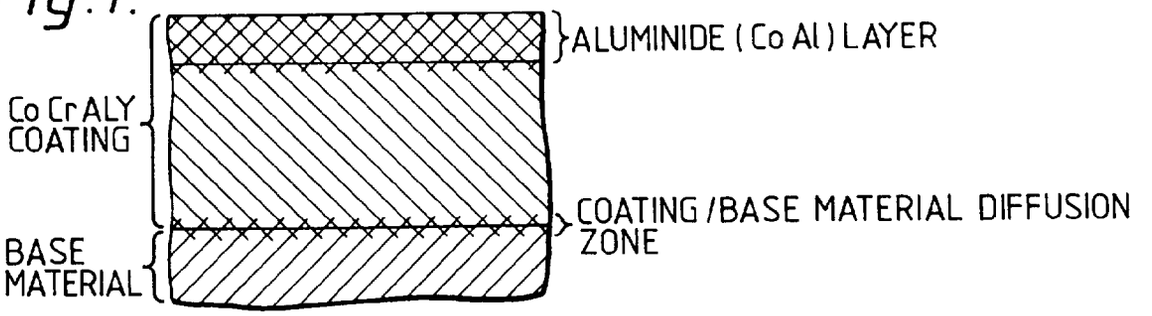


Fig.2.

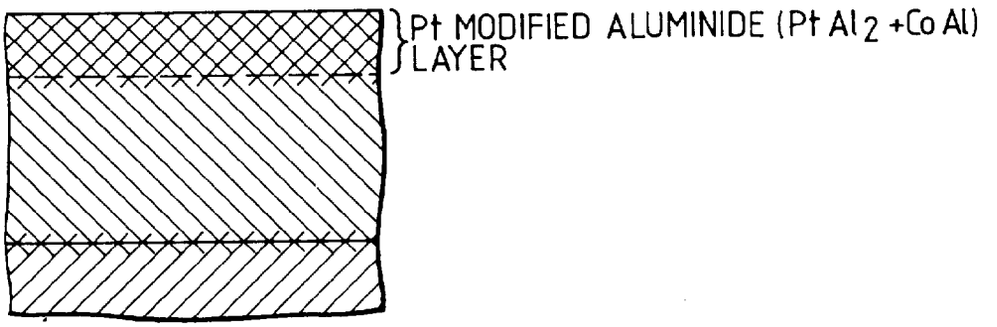


Fig.3.

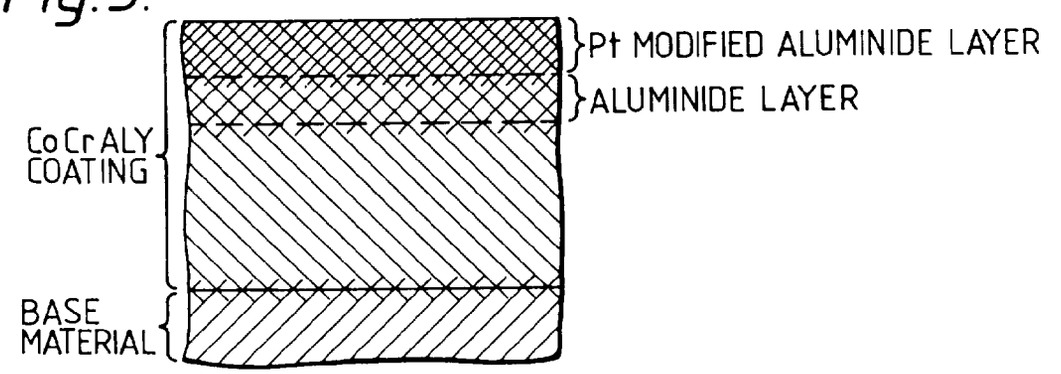


Fig. 4.

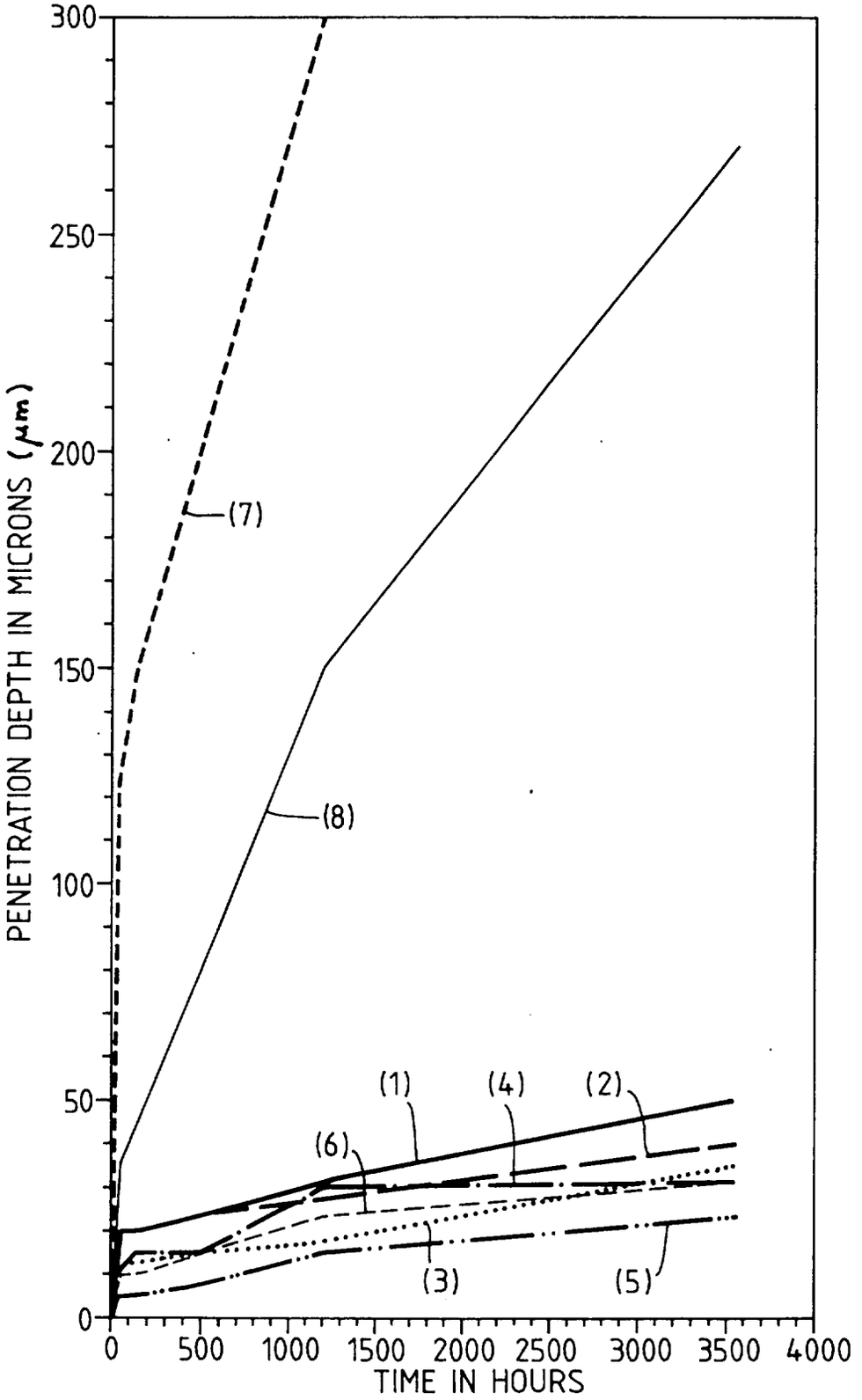

300
250
200
150
100
50
0
PENETRATION DEPTH IN MICRONS (μm)
0
500
1000
1500
2000
2500
3000
3500
4000
TIME IN HOURS
(7)
(8)
(1)
(4)
(2)
(6)
(3)
(5)

Fig. 5.

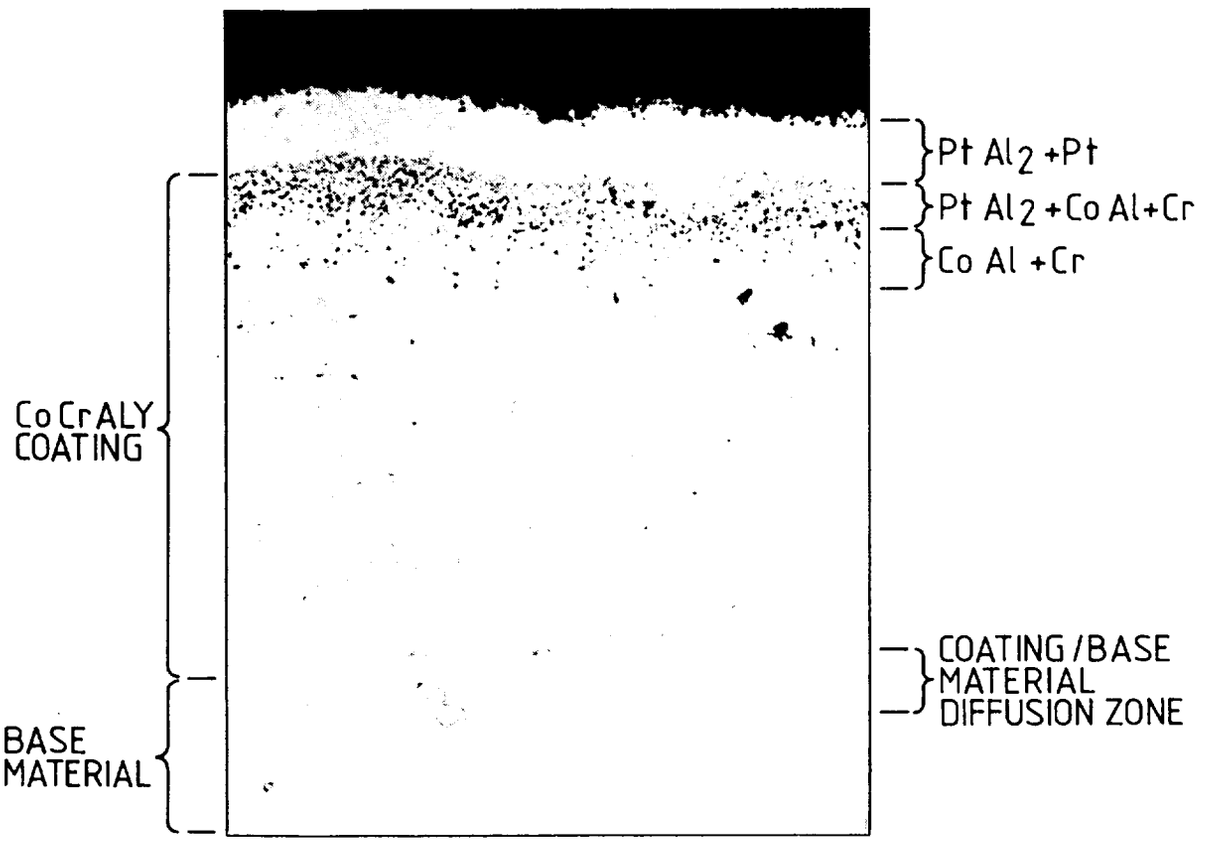
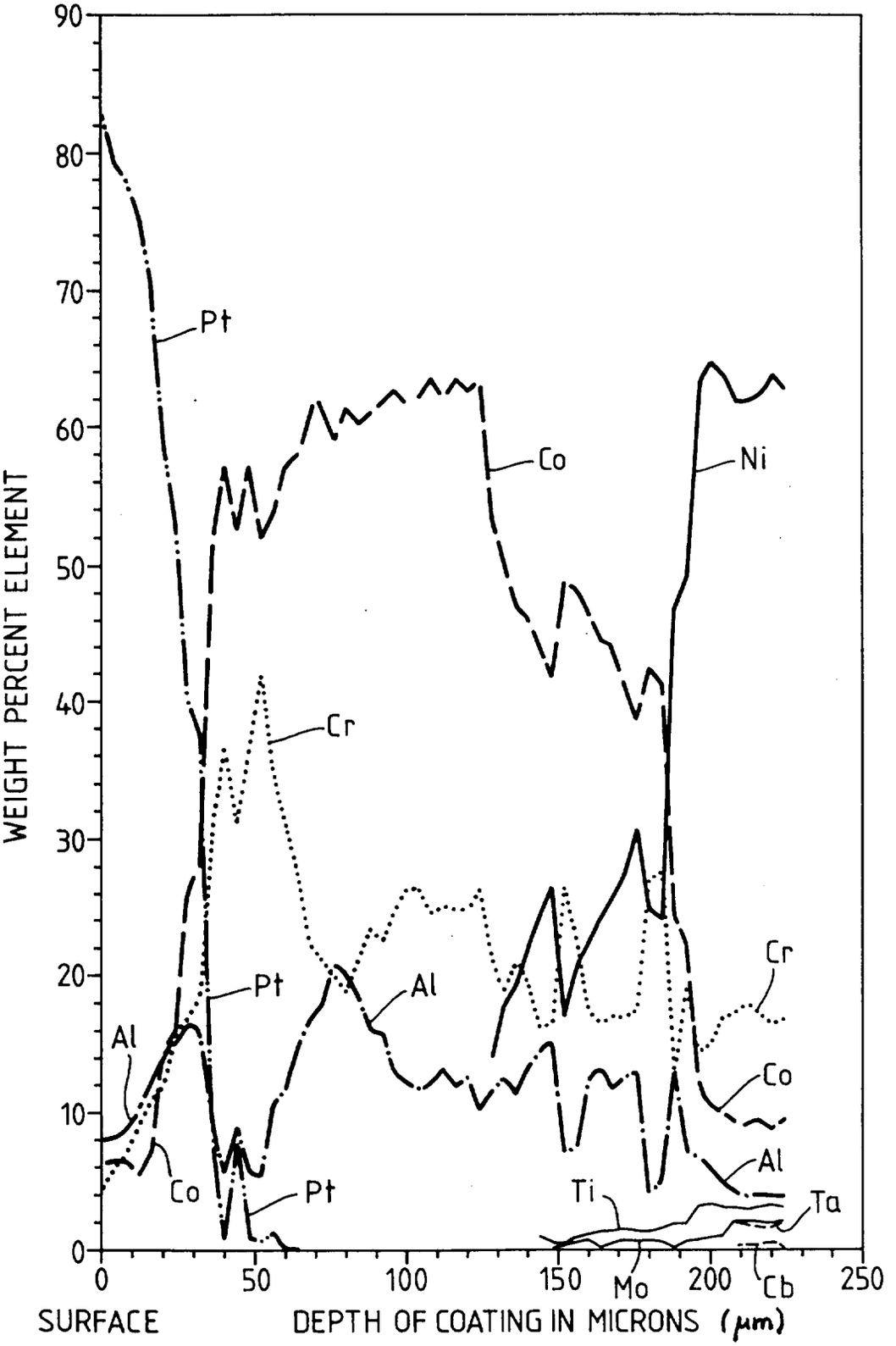

Pt Al2 +Pt
Pt Al2 +Co Al+Cr
Co Al +Cr
CoCrALY COATING
BASE MATERIAL
COATING/BASE MATERIAL DIFFUSION ZONE

Fig. 6.


WEIGHT PERCENT ELEMENT
90
80
70
60
50
40
30
20
10
0
Pt
Co
Ni
Cr
Pt
Al
Al
Cr
Co
Co
Pt
Al
Ti
Ta
Mo
Cb
0
50
100
150
200
250
SURFACE
DEPTH OF COATING IN MICRONS (μm)