

APPLICATION FOR A STANDARD PATENT OR A STANDARD PATENT OF ADDITION

LODGED AT SUB-C
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Melbourne
80688/87

596877

Insert full
name(s) of
applicant(s)

Insert address(es)
of applicant(s)

Insert title
of invention

(tick appropriate
box)

Insert name of
actual inventor

Insert address
for service of
notices in
Australia

for Convention
cases only

- (71) I/We UNITED TECHNOLOGIES CORPORATION
of 1, Financial Plaza, United Technologies Building, Hartford, Connecticut
06101, United States of America
- (54) hereby apply for the grant of a ☒ standard patent ☐ patent of addition for an invention entitled METHOD FOR APPLYING ALUMINIDE COATINGS TO SUPERALLOYS
which is described in the accompanying ☐ provisional ☒ complete specification.
- (72) The actual inventor(s) of the said invention is/are MICHAEL STEPHEN MILANIAK,
WALTER E. OLSON, CLARK TATSUMI OKAWA
- (74) My/our address for service is SANDERCOCK, SMITH & BEADLE, 207 Riversdale Road,
(P.O. Box 410) Hawthorn, Victoria, 3122 Attorney Code SA

(ONLY TO BE USED IN THE CASE OF A CONVENTION APPLICATION)

Details of basic application(s) —

NUMBER	COUNTRY	DATE OF APPLICATION	ISO Code
926273	United States of America	3 November 1986	US
PATENT OFFICE 831123 Collector of Public Monies APPLICATION ACCEPTED AND AMENDMENTS ALLOWED <u>23-2-90</u>			

Insert day, month
and year form
signed

Dated this 2nd day of November, 19 87

UNITED TECHNOLOGIES CORPORATION

Signature of
applicant or
Australian
attorney

TO

(Signature)
SANDERCOCK, SMITH & BEADLE

THE COMMISSIONER OF PATENTS

This form must be accompanied by either a provisional specification (Form 9 and true copy) or by a complete specification (Form 10 and true copy).

Australia Patent Declaration Form

Forms 7 and 8

AUSTRALIAPatents Act 1952DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITIONName(s) of
Applicant(s)In support of the application made by UNITED TECHNOLOGIES
CORPORATION

Title

for a patent for an invention entitled METHOD FOR APPLYING
ALUMINIDE COATINGS TO SUPERALLOYSName(s) and
address(es)
of person(s)
making
declaration~~I/we~~, Stephen E. Revis of 4 Mountain View Drive, West Hartford,
Connecticut 06117, USA

do solemnly and sincerely declare as follows:-

1. ~~I am/we are the applicant(s) for the patent, or~~
~~am/are~~ authorised by the abovementioned applicant
to make this declaration on its behalf.2. The basic application(s) as defined by Section 141
of the Act was/~~were~~ made in the following country
or countries on the following date(s) by the
following applicant(s) namely:-Country, filing
date and namein the United States of America on November 3 1986

of Applicant(s)

~~by~~

For the or

~~in~~each basic
application~~on~~ 19by Walter E. Olson, Michael S. Milaniak and Clark T. Okawa3. The said basic application(s) was/~~were~~ the first
application(s) made in a Convention country in respect
of the invention the subject of the application.Name(s) and
address(es)
of the or
each actual
inventor4. The actual inventor(s) of the said invention ~~is/are~~
Walter E. Olson of 46 Winding Brook Trail, Vernon, Connecticut 06066,
USA; Michael S. Milaniak of 24 Way Road, Middlefield, Connecticut
06455, USA; and Clark T. Okawa of 78 Honeypot Road, West Haven,
Connecticut 06516, USASee reverse
side of this
form for
guidance in
completing
this part5. The facts upon which the applicant(s) is/~~are~~ entitled
to make this application are as follows:-
The said United Technologies Corporation is the assignee of the
said inventors.DECLARED at East Hartford, CT this 8th day of October 1987
USAUNITED TECHNOLOGIES CORPORATION

By

Stephen E. Revis
Assistant Patent Counsel

(12) PATENT ABRIDGMENT (11) Document No. AU-B-80688/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 596877

(54) Title
METHOD FOR APPLYING ALUMINIDE COATINGS TO SUPERALLOYS

International Patent Classification(s)
(51)⁴ **C23C 024/08**

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(22) Application Date : **02.11.87**

(30) Priority Data

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926273	03.11.86	US UNITED STATES OF AMERICA

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(71) Applicant(s)
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(74) Attorney or Agent
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(57) Claim

1. A method for forming an aluminide coating on the surface of a substrate selected from the group consisting of nickel and cobalt base alloys, the method comprising the step of heating the substrate in the presence of a powder mixture ^{comprising} ~~consisting~~ ~~essentially of~~ a source of aluminum, a halide activator, and a buffer effective to control the activity of said aluminum source such that aluminum diffuses into the substrate and forms an outward diffusing aluminide coating, said powder mixture being substantially free of aluminum oxide.

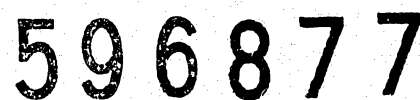
9. A method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy article, comprising the step of heating the article and a powder mixture ^{comprising} ~~consisting essentially of~~ cobalt aluminum, ammonium bifluoride and an effective amount of chromium metal to form an outward diffusing aluminide coating, the powder mixture being substantially free of aluminum oxide.

11. A method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy

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article, comprising the steps of disposing the article in out-of-contact relation with a powder mixture which, ^{comprising} ~~consists essentially of about~~, by weight percent, 5-20 $\text{NH}_4\text{F} \cdot \text{HF}$, 10-30 Cr, up to 10 Al_2O_3 , balance Co_2Al_5 , and heating the powder mixture to cause diffusion of aluminum into the article surface.



Form 10

COMPLETE SPECIFICATION

FOR OFFICE USE

Class

Int. Class

Application Number:
Lodged:

Complete Specification—Lodged: _____
Accepted: _____
Published: _____

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

TO BE COMPLETED BY APPLICANT

Name of Applicant: UNITED TECHNOLOGIES CORPORATION

Figure 6

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Complete Specification for the invention entitled:

METHOD FOR APPLYING ALUMINIDE COATINGS TO SUPERALLOYS

The following statement is a full description of this invention, including the best method of performing it known to me:—

5 This invention relates to aluminide coatings,
and in particular, to gas phase aluminide coatings.

Background

10 Aluminide coatings provide protection against
oxidation and corrosion degradation to nickel and
cobalt base superalloy articles used in gas turbine
engines. U.S. Patents which are indicative of the
skill in the art relative to aluminide coatings
include the following: 3,079,276, 3,276,903,
3,667,985, 3,801,353, 3,837,901, 3,958,047,
4,132,816, 4,142,023, 4,148,275 and 4,332,843. In
15 general, aluminide coatings are formed by heating a
powder mixture containing a source of aluminum, an
activator, and an inert buffer or diluent, in the
presence of the article to be coated. The article
may either be embedded in the powder mixture (and
20 the process is termed a "pack cementation" process)
or the article is suspended in out-of-contact
relation with the powder mixture (and the process is
termed a "vapor phase" process).

25 The source of aluminum may be pure aluminum
metal or it may be an alloy or intermetallic
containing aluminum, such as Co_2Al_5 , as disclosed in
U.S. Patent No. 4,132,816 to Benden et al.; U.S.
Patent No. 3,958,047 to Baldi discloses the use of
 Ni_3Al as the source of aluminum; and U.S. Patent No.

4,332,843 to Ahuja discloses the use of Fe_2Al_5 . Activators which have been used in the aluminiding process generally include halides of alkali or alkaline earth metals. See, e.g., the
5 aforementioned patent to Benden. Aluminum oxide is the typical diluent added to the powder mixture and controls the aluminum activity of the mixture. Aluminum oxide also prevents the powder mixture from sintering together during the coating process, as
10 discussed in U.S. Patent No. 3,667,985 to Levine et al.

Three problems which have been prevalent, especially in the gas phase aluminiding processes, are the formation of cryolite, Na_3AlF_6 , on the
15 surface of the coated article; the aggregation of "zipper oxides" on the original substrate surface; and the formation of oxides within the coating itself. Cryolite has been found to accelerate the rate of base metal degradation. While cryolite
20 formation can sometimes be limited by using special aluminiding powder mixtures, the quality of the coatings produced by such mixtures is considered to be not as good as the quality of the coatings produced by powder mixtures that result in cryolite
25 formation. Oxides at the coating-substrate interface, and within the coating itself are undesired, since they also degrade coating properties. The former types of oxides can cause exfoliation of the coating; the latter type can act
30 as fatigue initiation sites and sites for accelerated oxidation degradation.

Notwithstanding the advances made in the aluminiding field, researchers continue in their attempts to provide better coatings. Such coatings must have excellent resistance to oxidation and corrosion attack, and must be resistant to thermal fatigue. The present invention results from such effort.

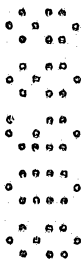
Disclosure of Invention

Improved ~~gas phase~~ aluminide coatings for nickel and cobalt base superalloys are formed by heating a powder mixture which includes a source of aluminum, a halide activator, and a buffer which is substantially free of aluminum oxide and which controls the aluminum activity in the powder mixture so that an outward diffusing aluminide coating is formed on the article. One powder mixture particularly useful in this invention consists essentially of about, by weight percent, 5-20 $\text{NH}_4\text{F} \cdot \text{HF}$, 10-30 Cr, balance Co_2Al_5 . Elimination of aluminum oxide as a powder constituent has been found to dramatically improve the quality of the aluminide coating produced. In particular, there is no cryolite formation on the coating surface, and oxide contamination at the coating-substrate interface and within the coating itself is essentially eliminated. The use of ammonium bifluoride, $\text{NH}_4\text{F} \cdot \text{HF}$, results in a coating mixture with excellent "throwing power", i.e., the ability to coat internal surfaces of hollow gas turbine blades. Chromium is used as a buffer to control the



aluminum activity, so that a thin, outward diffusing aluminide coating of about 0.0005-0.0035 inches is formed. Such thin coatings have excellent resistance to thermal fatigue, and have resistance to oxidation degradation which is comparable to the best prior art aluminide coatings.

Other features of the invention will become apparent to those skilled in the art from the following description and accompanying drawing.



10 Brief Description of the Drawing

Figure 1 is a photomicrograph of a prior art, inward diffusing aluminide coating; and

Figure 2 is a photomicrograph of a prior art, outward diffusing aluminide coating; and



15 Figure 3 is a photomicrograph of the outward diffusing aluminide coating of the invention.



Best Mode for Carrying Out the Invention

The invention is best understood by reference to the Figures. The inward diffusing prior art aluminide coating of Figure 1 is produced by a powder mixture which has a high aluminum activity. As seen in the Figure, the coating is characterized by a three zone microstructure with considerable phase precipitation in the NiAl rich outer zone.



20 While these types of coatings generally have good resistance to oxidation degradation, they range up to about 0.004 inches thick. Such thick aluminide coatings are known to have relatively poor thermal fatigue resistance.

The prior art coating shown in Figure 2 was produced with a powder mixture which contained about 60% by weight aluminum oxide as the diluent. The resulting contamination is clearly evident. The powder mixture had a comparatively lower aluminum activity than the mixture which produced the coating in Figure 1. As a result, the substrate basis metal (which is nickel in Figure 2, since the substrate is a nickel base superalloy) has diffused outwardly while the aluminum in the powder mixture diffused inwardly. The majority of the oxide contamination in Figure 2 are zipper oxides, i.e., oxides at the original substrate interface. As noted above, these oxides can cause the coating to spall during service use.

As is seen in Figure 3, the coating of the invention is an outward diffusing coating like the coating in Figure 2, but is significantly cleaner than the Figure 2 coating. This factor, in addition to the nominal 0.002 inch coating thickness, results in excellent oxidation resistance as well as resistance to thermal fatigue cracking.

The coating of the invention is produced in the following manner. A powder mixture consisting essentially of, by weight percent, 5-20 $\text{NH}_4\text{F.HF}$, 10-30 Cr, balance Co_2Al_5 is prepared. A nickel base superalloy article is suspended above the mixture and enclosed in a sealed retort similar to that shown in U.S. Patent No. 4,148,275 to Benden et al, the contents of which are incorporated by reference. The retort is heated to about 1,900-2,050°F, and

after between about two and twelve hours, a coating similar to that shown in Figure 3 is produced. The coating has a clean, uncontaminated interface, a metallographically distinguishable two-zone outward diffusing aluminide microstructure, and is about 0.0005-0.0035 inches thick, typically about 0.0015-0.0025 inches thick. It contains about 20-35 weight percent aluminum, along with elements from the substrate.

While Co_2Al_5 is the preferred source of aluminum, other sources may be used. Such sources include pure aluminum as well as transition metal alloys of aluminum (e.g., NiAl or Ni_3Al). A fluoride containing activator is preferred in the invention, since the use of such activators result in coating mixtures which have very good throwing power. Good throwing power is essential when a gas phase process is used to coat the internal surfaces of a hollow gas turbine engine blade. Ammonium bifluoride, $\text{NH}_4\text{F} \cdot \text{HF}$, is the preferred activator although halides (most preferably fluorides) of alkali or alkaline earth metals may also be useful. In the preferred embodiment, chromium is used as the diluent to control the activity of aluminum in the powder mixture; without the presence of chromium, the mixture will be too active, and a thick, inward diffusing coating would be produced. Elemental silicon may also be used as the buffer. Alloys or mixtures containing chromium and/or silicon may also be used. The powder mixture is substantially free from aluminum oxide, which is widely used as the

diluent in most prior art diffusion coating processes. It has been discovered that the presence of aluminum oxide in prior art coating mixtures is the apparent cause of the aforementioned undesired contamination (cryolite and entrapped oxides) which is typically observed in prior art gas phase aluminide coatings. According to the invention, aluminum oxide is removed from the powder mixture, which results in substantially cleaner (i.e., uncontaminated) coatings. While some small amounts of aluminum oxide (about 10% by weight, maximum) may be added to the powder mixture without causing an unacceptable amount of cryolite or oxides to form, the best aluminide coatings will be produced when the mixture is free of aluminum oxide. Powder mixtures containing no more than about 10 percent by weight of aluminum oxide are considered to be "substantially free" of aluminum oxide.

The preferred powder mixture of the invention consists essentially of 5-20 $\text{NH}_4\text{F}\cdot\text{HF}$, 10-30 Cr, up to about 10 Al_2O_3 , balance Co_2Al_5 . A preferred range is 7-17 $\text{NH}_4\text{F}\cdot\text{HF}$, 13-23 Cr, balance Co_2Al_5 . The most preferred powder mixture is about 12 $\text{NH}_4\text{F}\cdot\text{HF}$, 18 Cr, balance Co_2Al_5 . When nickel base superalloy articles in out-of-contact relation to this most preferred mixture are heated to about 1,975°F for about four hours, the resultant coatings are typically about 0.0015-0.0025 inches thick. They have comparable resistance to oxidation and corrosion attack as compared to prior art

coatings, and better resistance to thermal fatigue cracking.

5 From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various uses and conditions.

The claims form part of the disclosure of this specification.

XXXXXX

The claims defining the invention are as follows:

1. A method for forming an aluminide coating on the surface of a substrate selected from the group consisting of nickel and cobalt base alloys, the method comprising the step of heating the substrate in the presence of a powder mixture, ^{comprising} ~~consisting~~ ~~essentially of~~ a source of aluminum, a halide activator, and a buffer effective to control the activity of said aluminum source such that aluminum diffuses into the substrate and forms an outward diffusing aluminide coating, said powder mixture being substantially free of aluminum oxide.
2. The method of claim 1, wherein the source of aluminum is a transition metal alloy of aluminum.
3. The method of claim 2, wherein the source of aluminum is Co_2Al_5 .
4. The method of claim 1, wherein the activator is selected from the group consisting of fluorides of alkali and alkaline earth metals.
5. The method of claim 4, wherein the activator is $\text{NH}_4\text{F} \cdot \text{HF}$.
6. The method of claim 1, wherein the buffer is selected from the group consisting of chromium and silicon.



7. The method of claim 6, wherein the buffer is chromium metal or an alloy of chromium.

8. The method of claim 1, wherein the substrate is in out-of-contact relation with the powder mixture.

5 9. A method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy article, comprising the step of heating the article and a powder mixture, ^{comprising} ~~consisting essentially of~~ cobalt aluminum, ammonium bifluoride and an effective amount of chromium metal to form an outward diffusing aluminide coating, the powder mixture being substantially free of aluminum oxide.

10 10. The method of claim 9, conducted to produce a coating of ~~about~~ 0.0005-0.0035 inches.

15 11. A method for forming a gas phase aluminide coating on a nickel or cobalt base superalloy article, comprising the steps of disposing the article in out-of-contact relation with a powder mixture which, ^{comprising} ~~consists essentially of about~~, by weight percent, 5-20 $\text{NH}_4\text{F.HF}$, 10-30 Cr, up to 10 Al_2O_3 , balance Co_2Al_5 , and heating the powder mixture to cause diffusion of aluminum into the article surface.

20 12. The method of claim 11, wherein the powder mixture, ^{comprising} ~~consists essentially of about~~ 5-20 $\text{NH}_4\text{F.HF}$, 10-30Cr, balance Co_2Al_5 .



13. The method of claim 11, wherein the powder mixture, ^{comprising} ~~consists essentially of about~~ 7-17 $\text{NH}_4\text{F.HF}$, 13-23 Cr, balance Co_2Al_5 .

5 14. The method of claim 11, wherein the powder mixture, ^{comprising} ~~consists essentially of about~~ 12 $\text{NH}_4\text{F.HF}$, 18Cr, 70 Co_2Al_5 .

15. The method of claim 11, wherein the article and powder mixture are heated at ~~about~~ 1,900-2,050°F for about 2-12 hours.

16. A method for forming an aluminide coating, substantially as herein described.

17. A coating when produced by the method of any one of claims 1 to 16.

18. A coating substantially as herein described with reference to Fig. 3 of the accompanying drawings.

~~19. The articles, things, parts, elements, steps, features, methods, processes, compounds and compositions referred to or indicated in the specification and/or claims of the application individually or collectively, and any and all combinations of any two or more of such.~~

DATED THIS 2nd November, 1987

SANDERCOCK, SMITH & BEADLE

Fellows Institute of Patent

Attorneys of Australia.

Patent Attorneys for the Applicant

UNITED TECHNOLOGIES CORPORATION

