

PATENT SPECIFICATION

(11) 1 554 847

1 554 847

- (21) Application No. 16916/78 (22) Filed 28 Apr. 1978
 (31) Convention Application No. 835543 (32) Filed 22 Sep. 1977 in
 (33) United States of America (US)
 (44) Complete Specification Published 31 Oct. 1979
 (51) INT. CL.² C23C 9/02 13/02
 (52) Index at Acceptance
 C7F 1A 1B2 1B4 1V1 2A 2F 2G 2M 2N
 2P 2U 2V 3C 3D 4A 4E 4F 4K
 (72) Inventors: DAVID RONG-HWAN CHANG



(54) METALLIC COATED ARTICLE

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12345, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to metallic articles coated for improved environmental resistance, particularly hot corrosion resistance at elevated temperatures and, more particularly, to such articles having a complex graded coating interdiffused with the substrate.

The high temperature operating conditions of a gas turbine engine presented designers with a problem associated with component surface deterioration as a result of oxidation under such conditions. As a result, there have evolved a number of coating systems to protect the surfaces of those high temperature operating components such as turbine blades and vanes during operation in gas turbine engines. However, operation of such apparatus near or on bodies of salt water has presented additional problems associated with hot corrosion, the mechanism for which differs from oxidation.

It has been known for many years to improve environmental resistance of metallic articles through an aluminium or an aluminide coating. However, more recent efforts, which recognize the various types and interrelationships of surface oxides, have been reported. For example, U.S. Patent 3,996,021—Chang, issued December 7, 1976, recognizes the benefit of including in a surface coating the element Hf to provide HfO₂ for improved coating life. In addition, U.S. Patent 2,976,436—Chang, issued August 24, 1976, describes the benefits of including such elements as Pt, Rh and Pd along with Al and Hf for improved environmental resistance. Additional benefit has been disclosed in U.S. Patents 3,874,901 and 3,998,603 Rairden, III, through the use of an overlayer of aluminum.

The present invention provides a metallic article comprising (a) a substrate of a superalloy based on Fe, Co or Ni, and (b) a graded coating diffused with said substrate to increase the hot corrosion resistance of the substrate, characterized in that the graded coating consists of:

(i) an inner coating portion adjacent to and diffused with the substrate, and including predominantly Al, Cr and at least one element selected from Fe, Co and Ni, with the balance elements diffused from the substrate and the outer coating portions and

(ii) an outer coating portion adjacent to and diffused with the inner coating portion, and including 5-50 weight percent of elements selected from Hf, Pt, Rh and Pd, with the balance elements diffused from the inner coating portion.

Thus, the present invention provides a metallic article including a superalloy substrate based on an element selected from Fe, Co and Ni and into which is diffused a graded coating to increase hot corrosion resistance, as well as to provide good oxidation resistance, at elevated temperatures. The diffused, graded coating includes an inner coating portion adjacent to and diffused with the substrate, and including predominantly Al, Cr and at least one element of the group Fe, Co and Ni, along with elements diffused from the substrate and the outer coating portion. Adjacent to and diffused with the inner coating portion is an outer coating portion which includes 5-50 weight percent of at least one element from the group Hf, Pt, Rh and Pd, along with elements diffused from the substrate and the inner coating. In one form, the inner coating portion consists essentially of, by weight, 8-30% Al, 10-50% Cr, up to 10% Hf, up to 30% of elements selected from Pt, Rh and Pd, up to 3% Y, with the balance selected from the substrate elements, predominantly Fe, Co and Ni.

(16)

In one preferred form, the diffused outer coating portion consists essentially of, by weight, 2-5% Hf and 5-40% Pt along with elements diffused from the inner coating portion. In a preferred form, the inner coating portion consists essentially of, by weight, 8-20% Al, 10-40% Cr, up to 5% Hf, up to 20% Pt, up to 2% Y, with the balance at least one element selected from Fe, Co and Ni.

Recent emphasis on coatings for high temperature environmental protection of the superalloy articles has been on the MCrAlY-type coating in which the 'M' is at least one of the transition triad elements Fe, Co and Ni. One useful range for such a coating, as shown by the above-identified, patents, is, by weight 8-30% Al, 10-50% Cr, up to 3% Y with the balance at least one of the M elements. Such coatings have been reported as being applied to a substrate by a variety of methods including physical vapour deposition, flame or plasma spraying, sputtering, electron beam deposition etc. After such deposition, the coating can be diffused with the substrate.

In the above-identified Patent 3,874,901—Rairden, III it was recognized that the provision of a multiportion coating system provided improved environmental resistance through the use of an aluminizing overcoating. The present invention provides a significant improvement on such known systems or coatings through the provision of a graded coating of improved multiple portions. The inner portion provides the MCrAl-base type diffused alloy and an outer portion of the coating adjacent to and diffused primarily with the inner portion includes 5-50% weight percent of the elements Hf, Pt, Rh and Pd, shown to provide significant improvements over a single-coating portion as defined in the above Patents 3,976,436 and 3,996,021. More specifically, it has been recognized through the present invention that through use of an overlayer or outer coating portion including 5-50 weight percent of the elements Hf and Pt, a significant improvement in hot corrosion resistance is provided. This is achieved after interdiffusion between the substrate, the inner portion and the outer portion, creating a regenerating outer barrier of interrelated oxides which continue, during high temperature operation of the coated article, to provide significant hot corrosion resistance along with good oxidation resistance. The article of the present invention is partially dependent on the formation of dense α -Al₂O₃ to resist degradation. However, under hot corrosive environments, in addition to the spallation of α -Al₂O₃, there are at least two additional factors which cause faster degradation of the coating. One is the fluxing of Al₂O₃ by molten salt, the other is the rapid diffusio and reaction of sulfur through scale and coating materials. Using an Hf or Pt, or both, overlay the availability of Al, diffused from the inner coating portion, to reform Al₂O₃ is enhanced by increasing Al activity. The addition of Hf and Pt improves the Al₂O₃ scale adherence as well as its salt fluxing resistance. Both concepts have been demonstrated to be effective by the test results.

The coating associated with the present invention is defined as a 'graded' coating in that the concentrations of the various elements vary from the substrate through the inner coating portion and through the outer coating portion as a function of the degree of interdiffusion between the substrate and such portions. Thus, after diffusion, the inner coating portion is predominantly of the MCrAl-base type and the outer coating portion is 5-50 weight percent of the elements Hf, Pt, Rh and Pd, each along with an amount of other elements depending on their diffusion between the substrate and the inner and outer coating portions.

During the evaluation of the present invention, a variety of coating combinations were evaluated. The following Table I provides preferred composition ranges for the coating portions after interdiffusion. The graded inner coating portion was selected from the range, by weight, of 8-30% Al, 10-50% Cr, up to 10% Hf, up to 30% of at least one element selected from Pt, Rh and Pd, up to 3% Y with the balance predominantly at least one of the elements Fe, Co and Ni. The graded outer portion was not included in one example, was included as predominantly Al in another and, representative of the present invention, an example included, by weight, Pt in the range of about 20-40% Hf in the range of 2-5%.

Table I
Diffused Coating Compositions (Wt.%)

Example	Graded Inner Portion				Graded Outer Portion			
	Bal	Cr	Al	Y	Al	Pt	Hf	Bal
1	Co	20-30	9-16	.02-.05				
2	Co	20-30	9-16		10-50			*
3	Co	20-30	9-16			20-40	2-5	*

*Balance diffused from inner costing and substrate.

Table II

Cyclic Dynamic Hot Corrosion Life

1700°F/5 ppm sea salt solution

Total coating thickness: 4 mils

Substrate Alloy Ni-Base Rene' 80 Alloy

Diffused, Graded

Coating (Example)

Nominal Life

(hrs)

1200

2000

>3000

Table III

Hot Corrosion and Oxidation Data

Coating attack (in mils) after 1000 hrs.

Diffused, Graded

Coating (Example)

Hot Corrosion

1700°F

Oxidation

2000°F

1

3

15

2

2

12

3

0.2

6

The data of the above Tables II and III show the improved environmental resistance of the present invention through a comparison of its hot corrosion life and oxidation data with known coated articles. The present invention is represented by the Example 3 composition from Table I. The known coatings are represented by a CoCrAlY-type single-portion coating (Example 1), a CoCrAl-type coating with an aluminium overcoating of the type described in the above-referenced 3,874,901—Rairden, III (Example 2). The known coatings and that associated with the present invention were applied to test specimens of a nickel-base alloy, sometimes referred to as Rene' 80 nickel-base superalloy consisting nominally, by weight, of 0.15% C, 14% Cr, 5% Ti, 0.015% B, 3% Al, 4% W, 4% Mo, 9.5% Co, 0.06% Zr with the balance Ni and incidental impurities. In order to simulate gas turbine engine operating conditions in the vicinity of bodies of salt water, the cyclic dynamic test employed a 5 ppm sea salt solution. Such test involved exposing the specimens at 1700°F while, once an hour, cooling the specimens rapidly to 500°F for about one minute before recycling them to 1700°F. The inner or first coating portion, which is of the MCrAl-base type, was applied to the test specimens, in each example by physical vapour deposition. In Example 2, Al in the outer portion was applied through the use of a pack coating process of the type generally described in U.S. Patent 3,667,985—Levine et al, issued June 6, 1972, with the pack ingredients being varied, as is well known in the art, to provide the composition desired. It should be understood, however, that a variety of methods, some of which are mentioned above, can be used to apply the various coating portions.

The coating system of Example 3 in Table 1 was applied by first depositing CoCrAl through physical vapour deposition. Then the article thus coated was placed in a powder pack of the type described in the above Patent 3,996,021—Chang et al in which the element Hf was at present. Then Pt was applied through sputtering.

With reference to Table II, it can be seen that the coating of Examples 1 and 2, representing known coating systems, have a significantly lower hot corrosion life than does the graded coating system of the present invention, represented by Example 3 from Table I.

The unexpected and unusual results in environmental resistance through the present invention is further demonstrated by the data of Table III, representing both hot corrosion and oxidation data. In that Table, a comparison is shown between the known coating systems represented by Examples 1 and 2 with articles coated according to the present invention represented by Example 3. The remarkable improvement in hot corrosion resistance as well as improvement in oxidation resistance is easily recognized by those skilled in the art. The data of Table III were obtained in a hot corrosion evaluation at 1700°F using a jet engine fuel, identified as JP5 fuel, along with 5 ppm sea salt injection. The specimens were heated and cycled as described above in connection with Table II. The oxidation data were obtained using natural gas combustion to expose the specimens to 2000°F while, six times per hour, cooling the specimens rapidly to 700°F for about one minute before recycling to 2000°F.

WHAT WE CLAIM IS:

1. A metallic article comprising (a) a substrate of a superalloy based on Fe, Co or Ni, and (b) a graded coating diffused with said substrate to increase the hot corrosion resistance of the substrate, characterized in that the graded coating consists of:

(i) an inner coating portion adjacent to and diffused with the substrate, and including



1,554,847

3

Table II

Cyclic Dynamic Hot Corrosion Life

1700°F/5 ppm sea salt solution

Total coating thickness: 4 mils

Substrate Alloy Ni-Base Rene' 80 Alloy

Diffused, Graded

Coating (Example)

Nominal Life

(hrs)

1200

2000

>3000

Table III

Hot Corrosion and Oxidation Data

Coating attack (in mils) after 1000 hrs.

Diffused, Graded

Coating (Example)

Hot Corrosion

1700°F

Oxidation

2000°F

1

3

15

2

2

12

3

0.2

6

The data of the above Tables II and III show the improved environmental resistance of the present invention through a comparison of its hot corrosion life and oxidation data with known coated articles. The present invention is represented by the Example 3 composition from Table 1. The known coatings are represented by a CoCrAlY-type single-portion coating (Example 1), a CoCrAl-type coating with an aluminium overcoating of the type described in the above-referenced 3,874,901—Rairden, III (Example 2). The known coatings and that associated with the present invention were applied to test specimens of a nickel-base alloy, sometimes referred to as Rene' 80 nickel-base superalloy consisting nominally, by weight, of 0.15% C, 14% Cr, 5% Ti, 0.015% B, 3% Al, 4% W, 4% Mo, 9.5% Co, 0.06% Zr with the balance Ni and incidental impurities. In order to simulate gas turbine engine operating conditions in the vicinity of bodies of salt water, the cyclic dynamic test employed a 5 ppm sea salt solution. Such test involved exposing the specimens at 1700°F while, once an hour, cooling the specimens rapidly to 500°F for about one minute before recycling them to 1700°F. The inner or first coating portion, which is of the MCrAl-base type, was applied to the test specimens, in each example by physical vapour deposition. In Example 2, Al in the outer portion was applied through the use of a pack coating process of the type generally described in U.S. Patent 3,667,985—Levine et al, issued June 6, 1972, with the pack ingredients being varied, as is well known in the art, to provide the composition desired. It should be understood, however, that a variety of methods, some of which are mentioned above, can be used to apply the various coating portions.

The coating system of Example 3 in Table 1 was applied by first depositing CoCrAl through physical vapour deposition. Then the article thus coated was placed in a powder pack of the type described in the above Patent 3,996,021—Chang et al in which the element Hf was at present. Then Pt was applied through sputtering.

With reference to Table II, it can be seen that the coating of Examples 1 and 2, representing known coating systems, have a significantly lower hot corrosion life than does the graded coating system of the present invention, represented by Example 3 from Table I.

The unexpected and unusual results in environmental resistance through the present invention is further demonstrated by the data of Table III, representing both hot corrosion and oxidation data. In that Table, a comparison is shown between the known coating systems represented by Examples 1 and 2 with articles coated according to the present invention represented by Example 3. The remarkable improvement in hot corrosion resistance as well as improvement in oxidation resistance is easily recognized by those skilled in the art. The data of Table III were obtained in a hot corrosion evaluation at 1700°F using a jet engine fuel, identified as JP5 fuel, along with 5 ppm sea salt injection. The specimens were heated and cycled as described above in connection with Table II. The oxidation data were obtained using natural gas combustion to expose the specimens to 2000°F while, six times per hour, cooling the specimens rapidly to 700°F for about one minute before recycling to 2000°F.

WHAT WE CLAIM IS:

1. A metallic article comprising (a) a substrate of a superalloy based on Fe, Co or Ni, and (b) a graded coating diffused with said substrate to increase the hot corrosion resistance of the substrate, characterized in that the graded coating consists of:

(i) an inner coating portion adjacent to and diffused with the substrate, and including

18



1,554,847

- 4
- predominantly Al, Cr and at least one element selected from Fe, Co and Ni, with the balance elements diffused from the substrate and the outer coating portions and
- 5 (ii) an outer coating portion adjacent to and diffused with the inner coating portion, and including 5-50 weight percent of elements selected from Hf, Pt, Rh and Pd, with the balance elements diffused from the inner coating portion. 5
2. An article as claimed in claim 1 in which the inner coating portion consists of, by weight, 8-30% Al, 10-50% Cr, up to 10% Hf, up to 30% of elements selected from Pt, Rh and Pd, up to 3% Y, with the balance at least one element selected from Fe, Co and Ni.
- 10 3. An article as claimed in claim 1 or claim 2 in which the outer coating portion includes 2-5% Hf and 5-40% Pt. 10
4. An article as claimed in claim 3 in which the outer coating portion includes 20-40% Pt.
5. An article as claimed in claim 2 in which the inner coating portion consists of, by weight, 8-20% Al, 10-40% Cr, up to 5% Hf, up to 20% of at least one element selected from Pt, Rh and Pd, up to 2% of Y with the balance at least one element selected from Fe, Co and Ni.
- 15 6. An article as claimed in claim 5 in which the Al is 9-16% and the Cr is 20-30%. 15
7. A metallic article which as claimed in claim 1 substantially as hereinbefore described in Example 3.

20 PAUL TURNER B.Sc.,
Agent for the Applicants,
Chartered Patent Agent,
9 Staple Inn,
London WC1V 7QH. 20