

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN METALLIC COATED ARTICLES

(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 have 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—recognises the benefit of including in a surface coating the element Hf to provide HfO₂ for improved coating life. In addition U.S. Patent 3,976,436 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 through the use of an overlayer of aluminum.

According to the present invention there is provided 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 characterised in that the graded coating consists of:

(i) an inner coating portion adjacent to and diffused with the substrate, and including predominantly 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 predominantly Al and at least one element 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 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 Cr and at least one element of the group Fe, Co and Ni, along with elements diffused from the substrate and outer coating portion. Adjacent to and diffused with the inner coating portion is an outer coating portion which includes predominantly Al and 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, which also includes Al, 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. In one form,

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the diffused outer coating portion consists essentially of, by weight, 10-50% Al, 1-40% of at least one element selected from Hf, Pt, Rh and Pd, along with elements diffused from the substrate and inner coating portion. In a more preferred form, the diffused outer coating portion consists essentially of, by weight, 10-30% Al, 2-5% Hf, 5-40% Pt, with the balance at least one of the substrate elements, predominantly Fe, Co and Ni. In another preferred form the diffused 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 MCr-base type diffused alloy and an outer portion of the coating adjacent to and diffused primarily with the inner portion includes predominantly Al and at least one of the elements Hf, Pt, Rh and Pd, shown to provide significant improvements over a single-coating portion as defined in Patents 3,976,436 and 3,996,021. More specifically, it has been recognized through the present invention that by combining Al with such elements as Hf and Pt, in the group identified above, in an overlayer coating, 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 diffusion and reaction of sulfur through scale and coating materials. The concept of using Al overlay along with such metal additions as Hf, Pt, Rh and Pd is to increase the availability of Al to reform Al₂O₃ by increasing Al activity. The addition of Hf improves the Al₂O₃ scale adherence as well as its salt fluxing resistance by forming a HfO₂ barrier. Both concepts have been demonstrated to be effective by the test results. The combination of Pt, Rh or Pd and Hf additions further improves the coating performance.

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 MCr-base type, preferably the MCrAl-base type, and the outer coating portion is predominantly Al and at least one 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 was evaluated. The following Table I provides the 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 some examples and in others was included as predominantly Al along with diffused elements. Representative of the present invention, some examples of the outer portion included, by weight, Al in the range of about 10-50% along with Hf in the range of 1-40% or Pt in the range of 1-40% or both, preferably 10-30% Al, and 2-5% Hf or 20-40% Pt or both.

Table I
Diffused Coating Compositions (Wt.%)

5	Example	Graded Inner Portion			Y	Graded Outer Portion			Bal	5
		Bal	Cr	Al		Al	Hf	Pt		
	1	Co	20-30	9-16	.02-.05					
	2	Co	20-30	9-16		10-50			*	
	3	Co	20-30	9-16		10-30	2-5		*	
	4	Co	20-30	9-16		10-30	2-5	20-40	*	
10	5	Ni	15-25	8-12	.1-.7					10
	6	Ni	15-25	8-12	.1-.7	10-50			*	
	7	Ni	15-25	8-12		10-30	2-5		*	
	8	Ni	15-25	8-12		10-30	2-5		*	
15	9	Fe	20-30	9-16		10-30	2-5			15

*Balance diffused from inner coating and substrate

Table II
Cyclic Dynamic Hot Corrosion Life
1700°F/5 ppm sea salt solution
Total coating thickness: 4 mils

Diffused, Graded Coating (Example)	Substrate Alloy Base	Nominal Life (hrs)
1	Ni(A)	1200
2	Ni(A)	2000
3	Ni(A)	>3000
3	Co(B)	>3000
4	Co(B)	>3000
(A) Rene' 80 alloy		
(B) X-40 alloy		

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
5	8	4
6	7	3
7	4	2
8	4	2
1	3	15
2	2	12
3	1	8
4	0.3	6
9	0.5	4

The above Table II presents the hot corrosion life of the present invention, represented by the composition of Examples 3 and 4 from Table I, compared with a CoCrAlY-type single portion coating (Example 1), and with a CoCrAl-type coating with an aluminum overcoating of the type described in the above-referenced 3,874,901—Rairden, III (Example 2). The present invention was 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; and to test specimens of a cobalt-base alloy sometimes referred to as X-40 cobalt-base superalloy, consisting nominally, by weight, of 0.5% C, 25.5% Cr, 7.5% W, 10% Ni, with the balance Co 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 MCr or MCrAl type, was applied to the test specimens, in each case except Example 8, by physical vapour deposition. In those examples including Al or Al and Hf in an outer coating, such elements were 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. The coating system of Example 4 in Table 1 was applied by the physical vapour deposition of CoCrAl followed by the application of Pt through sputtering. Then the article thus coated was placed in a powder pack of the type described in Patent 3,996,021—Chang et al in which both of the elements Al and Hf were present. The coating system of Example 8 in Table 1 was applied by electroplating a plurality of alternate layers of Ni and Cr on the substrate after which the Al and Hf were applied by the above-described powder pack process. 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.

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 Examples 3 and 4 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 5, 6, 1 and 2 with articles coated according to the present invention represented by Examples 7, 8, 9, 3 and 4. 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) a inner coating portion adjacent to and diffused with the substrate, and including predominantly 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 predominantly Al and at least one element selected from Hf, Pt, Rh and Pd, with the balance elements diffused from the inner coating portion.

2. An article as claimed in claim 1 in which the inner coating portion consists of, by weight, 10-50% Cr, up to 30% Al, up to 10% Hf, up to 30% of elements selected from the group consisting of Pt, Rh and Pd, up to 3% Y, with the balance at least one element selected from Fe, Co and Ni and the outer coating portion includes, by weight, 10-50% Al and 1-40% of elements selected from Hf, Pt, Rh and Pd.

3. An article as claimed in claim 2 in which the outer coating portion includes 10-30% Al plus 2-5 Hf and/or 20-40% Pt.

4. An article as claimed in claim 2 in which the outer coating portion includes 10-30% Al and 5-40% Pt.

5. An article as claimed in any one of claims 2 to 4 in which the inner coating portion consists 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.

6. An article as claimed in claim 5 in which the Al is 8-16% and the Cr is 15-30%.

7. A metallic article as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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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 Examples 3 and 4 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 5, 6, 1 and 2 with articles coated according to the present invention represented by Examples 7, 8, 9, 3 and 4. 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.

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(ii) an outer coating portion adjacent to and diffused with the inner coating portion, and including predominantly Al and at least one element selected from Hf, Pt, Rh and Pd, with the balance elements diffused from the inner coating portion.

2. An article as claimed in claim 1 in which the inner coating portion consists of, by weight, 10-50% Cr, up to 30% Al, up to 10% Hf, up to 30% of elements selected from the group consisting of Pt, Rh and Pd, up to 3% Y, with the balance at least one element selected from Fe, Co and Ni and the outer coating portion includes, by weight, 10-50% Al and 1-40% of elements selected from Hf, Pt, Rh and Pd.

3. An article as claimed in claim 2 in which the outer coating portion includes 10-30% Al plus 2-5 Hf and/or 20-40% Pt.

4. An article as claimed in claim 2 in which the outer coating portion includes 10-30% Al and 5-40% Pt.

5. An article as claimed in any one of claims 2 to 4 in which the inner coating portion consists 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.

6. An article as claimed in claim 5 in which the Al is 8-16% and the Cr is 15-30%.

7. A metallic article as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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