

[54] **CORROSION-RESISTANT COATING FOR SUPERALLOYS**

[75] Inventors: **Adrian M. Beltran**, Ballston Lake;
Norman R. Lindblad, Schenectady;
Gerald E. Wasielewski, Rexford, all
of N.Y.

[73] Assignee: **General Electric Company**,
Schenectady, N.Y.

[22] Filed: **June 17, 1974**

[21] Appl. No.: **479,853**

[52] **U.S. Cl.**..... **29/194; 75/134 F; 75/176**

[51] **Int. Cl.²**..... **B32B 15/04**

[58] **Field of Search**..... **29/194; 75/176, 171, 134 F**

[56] **References Cited**

UNITED STATES PATENTS

3,015,880 1/1962 Stephenson..... 29/194

3,155,491	11/1964	Hoppin et al.	75/171 X
3,649,225	3/1972	Simmons.....	29/194
3,754,968	8/1973	Reznik.....	29/194 X
3,810,754	5/1974	Ford et al.	75/171

Primary Examiner—L. Dewayne Rutledge

Assistant Examiner—E. L. Weise

Attorney, Agent, or Firm—John F. Ahern; James W. Mitchell

[57]

ABSTRACT

An oxidation and hot corrosion resistant alloy for coating a superalloy substrate. The surface coating composition comprises a nickel base alloy containing chromium and silicon.

4 Claims, No Drawings

CORROSION-RESISTANT COATING FOR SUPERALLOYS

BACKGROUND OF THE INVENTION

This invention relates to the coating of a superalloy substrate with an oxidation and hot-corrosion resistant surface coating alloy composition comprising a nickel base alloy containing chromium and silicon which alloy will be referred to hereinafter as AMB-2.

Hot-corrosion resistance is required for applications in turbines burning natural gas or uncontaminated light distillates or in contaminated environments involving combusted diesel, heavy distillates or residual oils.

Many protective alloy coatings for superalloy substrates are shown by the prior art. These coatings include the conventional aluminide coatings which have technical limitations which restrict the coating thickness resulting in an early deterioration of the coatings and further do not exhibit the superior hot corrosion resistance properties of the subject alloy coating, especially in a hot-corrosion operating environment. The subject coating alloy is also more economical in its initial processing than the alloys of the prior art. The field repair of components removed from service is simple and more economical since selected areas can be re-coated without need to mask or protect areas not requiring additional coating, as is the case of pack-aluminide or electron beam vapor deposited coatings.

In considering alloy coating compositions for superalloy substrates it was discovered that the alloy must exhibit the following characteristics:

1. Must be oxidation and hot-corrosion resistant over the temperature range 1400° to about 2000°F.

2. Must melt, wet and flow uniformly at some temperature below the incipient melting point of the superalloy substrate. Ideally, the vacuum brazing time/temperature cycle used to apply the coating alloy to the substrate should be compatible with the normal heat treatment cycle for the substrate.

3. Must be metallurgically stable, and compatible with the substrate alloy.

SUMMARY OF THE INVENTION

It is therefore, an object of my invention to provide a superalloy with a coating alloy which is oxidation and hot-corrosion resistant over a temperature range.

Another object is to provide an alloy coating that melts, wets and flows uniformly at some temperature below the incipient melting point of the superalloy substrate.

A further object is to provide an alloy which is metallurgically compatible with the substrate alloy and may be applied as a thick coating.

Briefly stated, the present invention relates to a coating alloy for a superalloy substrate having the following composition: Chromium 45-65%, Silicon 5-12%, Nickel-balance. All compositions are given in weight percent. A nominal coating composition as proposed by applicant may comprise 45% Chromium, 10% Silicon with the balance Nickel.

It is known that high Cr levels are the most effective deterrent to hot corrosion caused by Na and S— bearing atmospheres in the temperature range 1400°-1800°F. At these temperatures, greater than about 36% Cr is required to generate α -Cr precipitate. However, it should be noted that the content of chro-

mium should not be too high since the coating may become brittle over the range recited. The embrittlement is caused by the formation of excessive amounts of hard, body centered cubic α -Cr precipitate.

Similarly, silicon is beneficial for oxidation and hot corrosion resistance through the formation of SiO_2 . Silicon is used to control the melting and solidification behavior of the coating since the eutectic temperature in the pure Ni-Cr binary system occurs at 2450°F which is too high for most nickel based superalloy substrates.

The coating may be applied to the substrate by various methods including vacuum brazing, which is an established industrial technique. However, other conventional methods of applying the coating alloy to the superalloy substrate could be used such as the slurry, aerosol spray or plasma spray plus heat treatment and transfer tape methods. However, some methods should be avoided such as the vapor deposition method which yields a coating microstructure oriented normal to the substrate surface, thus establishing potential short-circuit diffusion paths e.g., grain boundaries, and growth defects for the introduction of corrosives such as sulphur and oxygen to the substrate. The resolidification structure of the subject vacuum brazed alloy is non-oriented, precluding this potential failure mode. Since the subject process involves the liquid and not the vapor state, greater segregation of the coating elements occurs. The present alloy takes advantage of this fact since the high chromium content produces α -Cr precipitate particles dispersed in γ -solid solution nickel matrix containing a high chromium level. The lower melting point Ni:Si eutectic phase is equally well dispersed throughout the coating during solidification.

Those parts of the present invention which are considered to be new are set forth in detail in the claims appended hereto. The invention, however, may be better understood and the advantage appreciated from a detailed description as follows:

DETAILED DESCRIPTION

A coating alloy was prepared using a nominal alloy composition comprised of 45% Chromium, 10% Silicon and the balance Nickel. Other compositions may be used falling within the range, supra. The substrate was prepared by mechanical abrading or by chemical cleaning plus electroplating a 0.2 to 1.0 mil layer of nickel thereon. The alloy used is in the form of a powder and is fabricated into a brazing transfer tape. The tape is comprised of -200 +325 mesh powder, held together with about 5% of an organic binder on a plastic backing sheet. A template of the desired shape to fit the substrate is cut from the transfer tape. The plastic backing is removed and the tape applied to the substrate.

Additional liquid brazing cement may be needed to firmly adhere the tape in place. The coated part is then subjected to the vacuum brazing cycle. The vacuum brazing cycle is controlled to permit outgassing of the binder at about 700° to 1000°F, to minimize contamination of the coating and substrate. The optimum vacuum brazing cycle consists of heating the alloy to a temperature of about 2075°F for about 5 minutes followed by argon gas cooling. Generally no finishing treatments are required, since the as-brazed coated surface yields a surface finish in the 35 to 60 microinch (RMS) range. The part may receive a final heat treatment to develop the mechanical properties of the sub-

strate. This step should be well below the alloy brazing temperature, to prevent re-melting of the coating or excessive interdiffusion of critical elements across the interface between the coating and substrate. Hence, the coating cycle must be included in the appropriate heat

taining brittle intermetallic compounds, such as sigma and carbides.

The nominal alloy compositions of the superalloy substrates to which our coating is applied are listed in Table A as follows:

Table A

Alloy	Nominal Alloy Compositions of Superalloy Substrates											
	Ni	Co	Cr	Al	Ti	Mo	W	Cb	Ta	B	Zr	C
IN-738	Bal.	8.5	16	3.4	3.4	1.75	2.6	0.9	1.75	0.01	0.04	0.11
IN-792	Bal.	9	12.5	3.5	4.1	1.9	4	(0.5 Hf)	4	0.015	0.013	0.13
Rene '77	Bal.	15	14	4.3	3.4	4.2	—	—	—	0.016	0.04	0.07
Rene '80	Bal.	9.5	14	3.0	5.0	4.0	4.0	—	—	0.015	0.03	0.17
MM-509	10	Bal.	23.5	—	0.2	—	7	—	3.5	—	0.5	0.6

treatment sequence for the specific substrate alloy.

In the as-solidified condition, the microstructure of the subject alloy contains a mixture of γ -Ni matrix, α -Cr precipitate particles, and Ni:Si eutectic. The precise composition and morphology of these phases depend both on the starting compositions of the subject alloy powder and substrate alloy, as well as the subsequent brazing and heat treatment cycles. The corrosion resistance of the subject alloy is derived from the high bulk Cr content (i.e. 45%) of the coating, but more specifically, it is due to the α -Cr particles and the high Cr, γ -Ni matrix, which constitute a very significant portion of the coated structure. Since the coating is applied in the liquid state and resolidified, elements from the substrate are easily incorporated into the coating. Hence, the brazing cycle (time and temperature) can be utilized to control the morphology and composition of the coating to some extent. Nickel base superalloys have been coated in the temperature range 2060° to 2130°F, with time-at-temperature between 2 and 20 minutes. Lower brazing temperatures are not preferred due to AMB-2's melting characteristics. Higher brazing temperatures can be used depending upon the heating and cooling rates, the equipment used and other considerations. Specific superalloy substrates may even require higher temperatures; however, the optimum parameters for the reference alloys is 2075°F for 5 minutes. In general, the higher the temperature, the shorter the time, to prevent excessive flow, reaction, and interdiffusion with the substrate. High temperatures and/or longer brazing times promote large α -Cr particles, less Ni:Si eutectic but greater interdiffusion with the substrate. Lower temperatures and time produce smaller, better dispersed α -Cr particles and Ni:Si eutectic, with little substrate interdiffusion. One feature of the subject alloy coating in the as-coated condition is its lack of a complex "diffusion zone" between the coating and substrate. By contrast, conventional aluminide coatings are characterized by a finger-like diffusion zone con-

The non-oriented structure of the subject alloy is due to the nature of the melting and re-solidification process. Segregation of the elements and resulting precipitates is related to composition, heat input during brazing, and cooling conditions. Line-of-sight vapor-deposited coatings, such as the MCrAlY's deposited by electron beam evaporation, generally grow normal to the substrate surface. Grain growth is, therefore, normal to the substrate, hence, growth defects are also oriented. Growth defects, when they occur in the subject alloy, are non-oriented solidification defects.

As previously stated, the subject alloy coating for a superalloy substrate has exhibited superior hot corrosion resistant properties over other prior art coated superalloys. Oxidation/hot-corrosion testing have been conducted under simulated gas turbine condition in a small combustion burner rig. A controlled atmosphere was produced by combusting doped diesel oil containing 1% S, to which artificial sea salt was mixed to produce 8 ppm Na in the combustion products. The rigs were run at 1600°F, at an air:fuel ratio of 60:1 with a gas velocity of 70 fps. The specimens were removed and air-blasted to room temperature every 50 hours to simulate turbine shutdown and to promote oxide and/or coating spallation under severe thermal cycling conditions. This is the most conditions test condition utilized to simulate a hot-corrosion operating environment.

In a first test AMB-2 was braze-coated on IN-738 using techniques previously described, and compared to available commercial aluminide coatings applied to IN-738. Results were obtained by sectioning the specimens, and metallographically determining at 100 times magnification the maximum depth of corrosion penetration through the coating and substrate, the average bulk coating surface loss, as well as an approximation of the area percent coating remaining. The results, listed in Table I below show the clear superiority of AMB-2 over conventional aluminide coatings.

Table I

Substrate Alloy	Coating	Fuel	Temp. °F	Time-Hr.	Max. Penetration Mils	Bulk Surface Loss, Mils	% Coating Remaining
IN-738	AMB-2	D.O.+S.S.	1600	620	3.3	3.3	60
				1202	2.0	2.0	75
				2010	2.5	2.5	70
	(1)RT-21			1012	6.9	1.1	NA
				2212	15.3	4.6	0
				307	6.5	0.5	0
	(2)MDC-1			600	6.1	1.3	60
				1006	9.7	2.3	20
				1992	14.0	4.0	NA

Table I—Continued

Substrate Alloy	Coating	Fuel	Temp. °F	Time-Hr.	Max. Penetration Mils	Bulk Surface Loss, Mils	% Coating Remaining
(3)MDC-9				635	4.5	1.6	60
				1006	9.4	3.0	0
				1274	9.8	4.2	NA

NA—Not analyzed.

(1)RT-21-Nickel base alloy of Chromalloy American Corp. contains 17–35% Al, 0–10 Cr, balance Ni and 5% of other incidental elements.

(2)MDC-1-Nickel base alloy of Howmet Corp. contains 17–35% Al, balance nickel and up to 10% of other incidental elements.

(3)MDC-9-Nickel base alloy of Howmet Corp. contains 17–35% Al, 0–10 Cr, balance nickel and 5% of other incidental elements.

It is important to note that the commercial process used for applying conventional aluminide coatings, known as pack concentration, has technical and economic limitations which restrict aluminide thickness to approximately 3 mils and somewhat less on Co-base superalloys. Since pack cementation is basically a vapor deposition process, applied thickness is time-dependent. AMB-2, however, can be applied up to about 10 mils thickness, with no change in the time/temperature vacuum brazing cycle. These data in Table I show that the aluminide coatings tested were essentially fully penetrated after just 600 to 1000 hours, with virtually no coating remaining. In many cases, significant corrosion of the IN-738 substrate resulted from the destruction of the coating.

The data in Table I further shows that a substantial portion of AMB-2 remains after 2000 hours of testing. This is due, in part, to the fact that AMB-2 can be applied in thicknesses up to about 10 mils, as stated above, with no change required in the technique or time/temperature parameters used in its application. Hence, AMB-2 offers both a more corrosion resistant alloy composition and increased coating thickness, both of which result in a longer life.

Another series of burner rig tests were conducted on AMB-2 coated Rene-77, (See Table II below) and compared to conventional aluminide coatings. Some of the tests were run in an undoped natural gas atmosphere, which produces a normal oxidizing environ-

ment. Aluminide coatings generally offer excellent resistance in this case, but suffer severe attack in the presence of S and Na contaminated atmospheres. This data in Table II, post, confirms the above information that AMB-2 is at least as protective as aluminide coatings in undoped environments, and is superior in contaminated environments.

Another measure of coating behavior is its effect on the mechanical properties of the substrate. (See Table III below). Two different effects are possible: (1) the coating alloy reacts metallurgically with the substrate producing harmful phases which embrittle the structure, or (2) the thermal treatment required to apply and stabilize the coating is incompatible with the substrate's heat treatment, hence degrading its mechanical properties.

In Table III, standard 0.252 inch diameter as-cast test bars of Rene-77 and IN-738 were braze coated with AMB-2, and tensile and rupture tested. The results are compared in Table III with aluminide-coated bars of these two alloys. Each coating/alloy combination was given the full heat treatment previously found optimal for that system. The data shows that the room temperature tensile properties of both IN-738 and Rene-77 are least affected by AMB-2. Yield strengths are 10 to 15% higher than the aluminide coatings, with only slightly less ductility. The latter is due in part to the greater thickness of AMB-2.

Table II

Alloy Substrate	Coating	Fuel	Temp. °F	Time-Hr.	Mils Thickness Coating Remaining
Rene-77	AMB-2	Diesel Oil + Sea Salt	1600	2483	3.3
	MDC-1		1600	135	0
	MDC-9		1600	1200	2.6
	AMB-2		1800	631	4.5
	MDC-1	Natural Gas	1800	600	1.2
	MDC-9		1800	600	3.0
	AMB-2		1800	1110	4.2
	MDC-1		1800	1000	1.5
	MDC-9	Natural Gas	1800	1000	3.0
	AMB-2		1900	1008	3.7
	MDC-1		1900	1000	1.5
	MDC-9		1900	1000	3.0

Table III

Mechanical Properties of Coated Alloys							
A) Tensile Properties (70°F)							
Alloy	Coating	UTS-ksi	0.2 Y.S., ksi	0.02 Y.S., ksi	% El.	% RA	
Rene-77	None	136.5	112.0	105.5	9.0	12.4	
	AMB-2	135.5	114.3	102.0	5.8	4.0	
	MDC-1	123.0	102.2	86.0	5.0	12.5	
	MDC-9	117.0	101.0	87.0	4.0	8.6	
IN-738	AMB-2	142.5	121.0	105.0	4.3	6.3	
	MDC-1	146.2	108.2	93.2	5.3	8.7	
	MDC-9	154.8	104.8	92.0	9.2	13.6	
B) Stress Rupture							
Alloy	Coating	Stress ksi	Temp. °F	Time Hr.	% El.	% Ra	P*
IN-738	AMB-2	15	1800	386.8	12.6	36.0	51.0
	MDC-1	15	1800	215.9	25.4	32.2	50.5
	MDC-9	15	1800	283.9	24.9	32.0	50.7
Rene-77	AMB-2	15	1750	484.7	5.7	7.2	50.1
	MDC-1	15	1800	235.3	5.4	10.6	50.6
	MDC-9	15	1800	150.2	5.8	12.6	50.1

*Where $P = T (20 + \log t) \times 10^{-3}$
In stress-rupture at 1800F/15 ksi, AMB-2 also produces superior results on IN-738. For Rene-77, the parameter P shows that AMB-2 is at least equivalent to aluminide coating MDC-9. It is necessary to use the Larson-Miller parameter for comparison, since AMB-2 was tested at a different temperature.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. An oxidation and corrosion resistant composite comprising a superalloy substrate and a coating alloy bonded thereto consisting essentially of the following elements in weight percent:

- Chromium - 40-65%
- Silicon - 5-12%
- Nickel - Balance

2. The coating alloy of claim 1 consisting essentially of 45% chromium 10% silicon and the balance nickel.

3. The alloy of claim 1 wherein the microstructure contains a mixture of γ -Ni matrix, α -Cr precipitate particles and Ni:Si eutectic.

4. The coating alloy of claim 1 wherein the thickness of the alloy coating composition for the superalloy may range up to 10 mils.

* * * * *