

[54] **DIFFUSION COATING OF JET ENGINE COMPONENTS AND LIKE STRUCTURES**

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Related U.S. Application Data

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1968, abandoned.

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[51] Int. Cl. **B32b 15/00, B32b 15/02, C23c 9/02**

[58] Field of Search **148/31.5, 34;**
29/183.5, 197; 117/107, 107 P, 170.2, 71

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[57] **ABSTRACT**

Greatly increased thermal fatigue cracking resistance of high temperature resistant base metals such as cobalt and nickel and their alloys used to fabricate jet engine components and like parts is realized by diffusion coating the base metal with chromium, silicon and aluminum in particular proportions to diffuse into the base metal to a uniform depth and distribution between and across intergranular boundaries in the base metal, enabling slowed initiation of thermal fatigue cracking in the diffusion coating as well as reduced corrosion in the base metal.

15 Claims, No Drawings

DIFFUSION COATING OF JET ENGINE COMPONENTS AND LIKE STRUCTURES

REFERENCE TO RELATED APPLICATION

This application is a continuation in part of our copending application Ser. No. 731,631 entitled "DIFFUSED COATING OF HIGH TEMPERATURE RESISTANT ALLOYS," filed May 23, 1968, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention has to do with improvements in thermal fatigue cracking resistance through diffusion coating of fabricated high temperature resistant metal and alloy parts to substantially increase the service life of such components and parts, in general through a more highly uniform diffusion and distribution of coating metals into the part base metal which may be nickel, cobalt or an alloy in which nickel or cobalt is the largest single ingredient.

While it is not widely recognized, it is nonetheless true that many of the technological advances and scientific feats which continue apace in modern times are largely dependent on progressive betterment of metal. The advent and commercial acceptance of jet aircraft transportation, for example, has been made possible by the development of alloys able to withstand heat and chemical stresses within a turbine engine. Further advances in this field, e.g., to more powerful and/or smaller power plants will be made or not depending on the availability of materials capable of meeting even more stringent demands during their operating lifetime.

2. Prior Art

High temperature resistant alloys so called super-alloys, have been refined through application, development and research to a high state of suitability for their intended usages, e.g. as turbine blades and nozzles for jet engines. Because of deficiencies in chemical resistance of the super-alloys, it has been the practice to surface modify the fabricated alloy component or part with a more chemically resistant, albeit perhaps less temperature resistant, metal composition. Temperature resistance herein refers to mechanical strength or resistance to mechanical deterioration at elevated temperatures, while chemical resistance refers to resistance to chemical deterioration, or to corrosion. These factors are, of course, highly interrelated, since one may be the cause or occasion of the other. Longer service life is, of course, the objective. Failure of the protective coating, undetected, may result in irreparable damage to the alloy component or part, particularly now that routine turbine engine inspection periods in some instances are 5,000 hours or more.

It is common practice to diffuse aluminum and chromium into the surface of a cobalt or nickel alloy component or part to form a corrosion resisting coating. Such coatings have been shown to have service lives between 1,000 and 2,500 hours per mil of thickness on turbine blades in jet engines.

While such diffusion coatings have been a great advance in the art, the service life of the coated parts is desirably even further lengthened. It has been observed that thermal fatigue cracking failure of the components, such as turbine blades and vanes may occur at thin edges of the part and at relatively regularly spaced intervals along the thin edge. Investigation of this fail-

ure phenomenon has revealed that the character of the diffusion coating in terms of uniformity of depth and distribution of coating components is of extreme importance to thermal fatigue cracking resistance and must be considered along with the anti-corrosion properties of the coating itself. For example, studies of nickel and cobalt base alloys which have been diffusion coated with diffusion packs comprising aluminum with or without chromium have revealed that the aluminum is usually maldistributed. Aluminum diffuses preferentially along grain boundaries which are commonly columnar in configuration and essentially normal to the thin trailing edge of the part of the diffusion coated surface of the superalloy part by entering the spaces between grains of the base metal, herein referred to as intergranular spaces, which lie angularly disposed to the advance of the diffusion coating. Not only does the incursive presence of aluminum in these intergranular spaces set up stresses which tend to propagate thermal fatigue and/or cracking corrosion, but the subsequent diffusion of aluminum from the grain boundaries leaves voids which may serve as initiation sites for fatigue and/or corrosion. Thus, it will be seen that the maldistribution of aluminum greatly foreshortens service life of diffusion coated superalloys, by both creating fatigue and corrosion attack initiation locations and by setting up paths of stress for the rapid propagation of cracks and/or corrosion into the base metal. The latter effect is pernicious since the component or part may be damaged beyond recovery and need to be replaced, unlike instances where only coating or surface failure is encountered.

SUMMARY OF THE INVENTION

Accordingly, it is a major objective of the present invention to provide nickel or cobalt metal or alloy structures for jet engines and like purposes having coatings affording greatly improved thermal fatigue cracking resistance and corrosion resistance for extended service life, up to 5,000 hours, and more, per mil and method of producing such structures.

It has now been discovered that increased service life in jet engine component structures is realized from oxidation, halide and sulfidation corrosion resistant coatings of aluminum and chromium, diffused into the cobalt or nickel base metal, which have silicon additionally diffused thereinto as hereinafter described, by virtue of the increased uniformity of the coating and the substantial elimination of voids in the coating or intergranular concentrations of aluminum in the base metal. Further, the structures exhibit greatly improved resistance to thermal fatigue cracking.

The achievement of longer periods of corrosion resistance and fatigue cracking resistance by virtue of the incorporation of silicon into an aluminum, chromium diffusion layer in a cobalt, nickel or cobalt base alloy is highly surprising since silicon coatings are glass brittle. The result is achieved because of the improved distribution of the aluminum in the coating caused by the presence of the hereinafter defined proportions of silicon. Primary among advantages flowing from the use of silicon according to the invention is a desirable alteration toward uniformity in the wearing characteristics of the protective diffusion layer and away from the void formation previously experienced with aluminum, chromium diffusion coatings, which in the past has led to premature failures, again owing to

the uniform distribution of the aluminum, avoiding localized absences and concentrations particularly in intergranular spaces. In fact, in the structures according to the invention, the intergranular spaces in the base metal beyond the metallographically defined coating are free of aluminum introduced by the coating procedure. Additionally, the diffusion layer is of demonstrably finer grain, productive of better wear character. It is also found that the new coated alloys have a blue coloration at invention levels of silicon content, which color is a convenient indication of adequate levels of silicon input into the alloy. Also highly useful is a variation in wearing behavior of the silicon-containing diffusion layer. This variation comprises a readily perceptible roughening of the surface occurring at approximately 60 percent of the service life of the protective coating. Thus worn coatings which could fail prior to the next regular inspection, can be timely replaced, avoiding destruction to the base metal and the structure itself.

In specific terms, the invention provides a jet engine component or like structure having improved resistance to thermal fatigue cracking comprising a high temperature resistant base metal having a highly chemically resistant diffusion coating layer comprising diffused, dispersed and well distributed chromium and aluminum, together with silicon sufficient to maintain the dispersed distribution of the aluminum throughout the surface coating. The corrosion resistant surface layer formed on the nickel or cobalt based base metal, is generally from 0.5 to 10 mils up to 20 mils in depth and desirably has a crystalline configuration stable at 1,750°F. The silicon is distributed, by diffusion, sequentially or simultaneously with the other metal components, through the structure coating layer usually in a weight ratio, relative to the chromium of 0.6 to 1.4. Chromium and aluminum content may vary widely with accordingly different results. Useful results may be obtained generally with diffusion coatings containing in the range of 3 to 30 weight per cent chromium, 10 to 30 weight per cent aluminum and 5 to 35 weight per

sequentially, independently or simultaneously with the aluminum and chromium diffusion, each of which may themselves be diffused in a separate step. The diffusion is typically carried out in a manner such that the alloy surface is heated to between 1,750° and 1,900°F in contact with a diffusion pack of suitable composition, with regard to diffusion time and temperature, and typically comprising in the range of 0.3 to 10 weight per cent aluminum, 3 to 40 weight per cent chromium and 5 to 35 weight per cent silicon; an activator such as halogen or halide and an inert filler such as a polyvalent metal oxide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Structure base metals which may be provided with thermal fatigue improving, corrosion resistant coatings in accordance with the invention include the high temperature resistant cobalt and nickel and cobalt and nickel based alloys. The terms "cobalt-based" and "nickel-based" herein refer to alloys in which cobalt or nickel, respectively, is the largest single ingredient, in weight per cent, although this is not necessarily a major weight portion of the entire alloy. Thus, for example, suitable cobalt base alloys include those composed by weight of cobalt (35-80 percent) and tungsten 0-25 percent, chromium 0-40 percent, iron 0-20 percent, and/or carbon 0-4 percent. Typical cobalt base alloys are given in the Table below. Among suitable nickel base alloys are those composed by weight of nickel 35-99.5, chromium 0-25, iron 0-20, manganese 0-2, molybdenum 0-20, cobalt 0-25, tungsten 0-5 as well as 0-20 of platinum, palladium, vanadium, aluminum, titanium, tantalum, columbium, boron and zirconium. Typical nickel base alloys are given in the Table below, in weight per cent.

Preferred alloys for heat resistance contain from 50 to 70 weight per cent of the base metal and appreciable amounts of metals such as tungsten and molybdenum. These alloys contain no more than 10 weight per cent tantalum. The coatings taught herein are particularly effective with these alloys. While not wishing volatile

Composition	C	Cr	Ni	Co	Mo	W	Ti	Al	B	Fe	Mn	Zr	Other
A.....	.05	12	Bal.		4.5		0.6	5.9	.010			.10	2.0 Cb
B.....	.15	15.4	Bal.	19.7		3.0	4.4	2.9	.013	.07	<.1	.03	1.8 Cb, 2.2 Ta
C.....	1.8	15.9	Bal.	8.5	1.8	2.6	3.5	3.4	.011	.10	.02	.11	0.9 Cb, 1.9 Ta
D.....	.60	24.0	10.0	Bal.		7.0	.2			1.5		.5	3.5 Ta
E.....	1.8	10.0	Bal.	15.0	3.0		4.7	5.5	.014			.06	1.0 V
F.....	.15	9.0	Bal.	10.0	2.5	10.0	1.5	5.5	.015			.05	1.5 Ta
G.....	.13	6.1	Bal.	7.5	2.0	5.8	1.0	5.4	.02			.13	9.0 Ta, .5 Cb, .4 Re, .4 Hf
H.....	.21	12.7	Bal.	9.0	2.0	3.9	4.2	3.2	.02			.10	3.9 Ta
I.....	.10	8.0	Bal.	10.0	6.0		1.0	6.0	.015				4.3 Ta
J.....	.45	21.0		Bal.		11.0							Cb+Ta 1.75

cent silicon and in the above ratio to the chromium present. Diffusion coating or surface impregnation of the alloy typically produces small variations in composition with depth. In the present invention, the outer portion of the surface layer may be relatively rich in silicon in which case the blue coloration is quite pronounced.

The invention further contemplates a method imparting thermal fatigue cracking resistance to these alloy structures which includes diffusing aluminum and chromium into the alloy surface in a manner providing a balanced distribution thereof i.e., a distribution free of grain boundary localized concentrations of aluminum and incorporating silicon into the alloy surface, to maintain the balanced distribution of aluminum, either

be bound to any particular theory of operation, it is base metals the addition of silicon in the recommended proportions to an aluminum, chromium diffusion coating on these alloys interferes with the conventional intermetallic formations i.e., formations of nickel aluminides and cobalt aluminides and facilitates incorporation (in addition to silicon and aluminum) of a significant amount of chromium in the coating. This coating then acts in a synergistic manner. During use exposure of the coating, a tightly adherent, substantially impervious oxide layer is developed on the diffusion coating, probably through spinel formations. It has been observed that localized etching or corrosion of the present surface coatings does not soon occur, indicating the substantial absence of concentrations of easily de-

graded nickel aluminides, which can be formed once the initial lattice distribution of the aluminum in the surface layer is broken down. It is believed too, that the silicon helps limit concentrating redistribution of the aluminum, even after disruption of the initial lattice arrangement, further contributing to improved wear characteristics. Concentration of aluminum in intergranular spaces is avoided along with the usual concomitant holes in the coating layer which are initiation sites for corrosion and fatigue attack. Metals such as tantalum which form volatile oxides at prospective normal use temperatures do not provide useful base metals since the absence of inherent chemical resistance such as is found in cobalt and nickel base metals precludes practically usable structures since a flaw free coating is rarely achieved and any flaw can cause catastrophic failure in a tantalum base part, through progressive oxidation and vaporization of the oxide.

The surface incorporation of aluminum, chromium and silicon into the base alloy metal is accomplished by diffusion from a pack. Pack diffusion is a well established metal surface treating technique and basically comprises heating one or more of the to-be-diffused metals in surface contact with the metal parts to be surface modified at elevated temperatures and usually for relatively extended periods in a suitable container such as a metal box. Conventionally, and in the application of the diffusion metals of this invention, an inert diluent is present in the box as is an activator or transport compound. Diffusion is carried out in a nonoxygen containing atmosphere.

The pack ingredients are relatively fine powders and may include, as the inert diluent any of the refractory materials available in powdered form, preferably about 50 to 350 U.S. mesh, e.g., various aluminum compounds including clays and aluminum oxides as well as zirconia and magnesia and other polyvalent metal oxides. The activator is generally a halogen or halogen precursor compound. Thus fluorine, chlorine, bromine and iodine per se and in salt form, particularly alkali and alkaline earth metal and ammonium salt forms from which they are readily releasable are useful as activators.

The metal components of the pack composition may be and preferably are elemental forms of the aluminum, chromium and silicon, suitably reduced to U.S. mesh sizes of 60-350 mesh, but may be other compounds similarly size reduced which released these elements e.g., transition metal compounds thereof particularly the ferro-compounds such as ferro-silicon.

The pack composition is widely variable and dependent on reaction conditions used. In a broad sense, a pack of diluent, activator and one metal diffusant in a wide range of proportions is suitable. Where all diffusant metals are applied sequentially, the pack may contain from 2% or less up to 70 percent by weight or more of the metal to be diffused, a trace amount of activator e.g., 0.1-3 percent by weight and the balance diluent such as aluminum oxide. Thus, useful pack compositions can contain 0-70 percent by weight of the diffusant metals provided at least one such metal is present in an amount of 2 percent by weight or greater. Where two or three of the diffusant metals are simultaneously incorporated in the alloy part surface, the pack composition will be adjusted appropriately. Pack compositions thus may comprise by weight silicon 8-35 percent, chromium 3-40 percent, aluminum 0.3-7 per-

cent, activator 0.1-3 percent and diluent, the balance.

In preferred practice, the pack composition in finely divided form, less than 100 mesh, is thoroughly mixed and fired in a treatment retort at 1800°F for 8 to 12 hours. After this initial "burn out" cycle, pack additions of activator may be made followed by packing parts to be treated in the composition disposed in a diffusion retort and placed in a furnace for heating at above 1,750°F for 8 to 12 and preferably 10 hours, and optimally not above 1,900°F for achieving most desirable crystalline patterns in the surface layer.

The heated parts are noted to have a definite blue color which has been found to be indicative of a surface sufficiently rich in silicon to have extraordinary resistance to sulfur-salt corrosion at elevated temperatures.

Surface layer compositions containing by weight 10-60 percent and preferably 10-30 percent aluminum, 3-30 percent and preferably 4-20 percent chromium and 2.5-70 percent and preferably 8-20 percent silicon may be obtained by variation of pack composition and diffusion time and temperature, as will be apparent to those skilled in the art.

In the present coatings the maintenance of a silicon/chromium ratio between 0.6 and 1.4 has been found to confer substantial performance improvements, specifically maximum service life through reduced corrosion and enhanced thermal fatigue cracking resistance.

The invention will be further described by the following Examples in which all parts and percentages are by weight.

EXAMPLE 1

A pack having the following composition:

Silicon — 35 percent

Chromium — 40 percent

Aluminum — 4 percent

Halogen activator — 0.2 percent

Aluminum oxide q.s. to — 100 percent

and having an average particle size less than 100 mesh was thoroughly mixed, introduced into a treatment retort and fired at 1800°F for 10 hours. The compound was then shifted and there was incorporated therein an additional 0.2 percent halogen activator. This composition was packed around nickel and cobalt-based parts to be coated in a metal box having provision for air exclusion. These parts contained between 50 and 70 percent of nickel or cobalt respectively. After retorting in a furnace at 1,800°F for 10 hours the parts were removed from the pack and cooled. The blue color was striking. Analysis showed 23 percent aluminum, 6 percent silicon and 4.5 percent chromium.

EXAMPLE 2

The procedure of Example 1 was duplicated in treating parts of an alloy of nickel which contained less than 10 parts each of tungsten, aluminum, cobalt, molybdenum, titanium and tantalum and trace amounts of boron and zirconium. The composition of the coating was the same as in Example 1.

Control I

The procedure of Example 1 is followed using pure tantalum parts, with the same coating composition as in the Example.

Testing

The diffusion coated parts were tested in an erosion test rig which exposed them to combustion gases of an oil burner fed jet fuel, artificial sea water and sulfur, to

simulate on an accelerated basis the corrosive environment of a gas turbine engine burning high sulfur fuel in a marine environment. In a series of tests the coated parts of Examples 1 and 2 were found to withstand exposures of thirty to fifty hours per mil of coating thickness. Since the erosion rig test is about 100 times more rigorous than actual use conditions, part life is thus 3,000 to 5,000 hours per mil of coating thickness. The Control I parts experience catastrophic failure after only a few hours, as the tantalum oxide volatilizes.

The mode of erosion too is interesting in that wear is generally uniform across the part surface and not localized. Moreover, at about 60 percent wear a detectable roughening of the surface occurs, which may be used as a guide to determine desirability of recoating a particular part; to avoid part failure or loss of repairability during subsequent service.

Control II

The procedure of Example 1 is duplicated but omitting the silicon from the pack composition. On testing in the erosion rig pitting due to localized etching occurs in as little as 10 hours followed by rapid failure as the alloy part is exposed through the coating to the corrosive gases.

The parts obtained in Example 1 were subjected to thermocycling to evaluate thermal fatigue cracking resistance. In this test the parts are subjected to rapid thermal cycling at temperatures up to 1,900°F and back to ambient temperature to produce thermal stresses in the parts. Typically the parts of Example 1 are free of cracking at up to between 900 and 1,000 cycles. Parts of the same base metal and diffusion coated, but without use of silicon (Control II) show cracking at only 225 to 250 cycles.

Control III

The procedure of Example 2 was duplicated but employing a pack composition as follows:

Silicon — 8.5 percent

Chromium — 3.0 percent

Aluminum — 0.5 percent

Halogen activator of Example 2 — 0.2 percent

Aluminum oxide q.s. to — 100 percent

Following diffusion coating elemental analysis of the coating showed aluminum 19 percent, chromium 4.5 percent and silicon 9.5 percent. The ratio of silicon to chromium was above 2 well beyond the highest recommended ratio of 1.4. Testing of the coated parts in the erosion rig shows a service life of 10–12 hours per mil which is well below the life obtained with the desirable Si/Cr ratios mentioned above. Nonetheless the coating wears evenly so that early pitting and other localized failures are not a predominant factor indicating that the silicon at these higher levels relative to chromium is operating to improve the performance characteristics of the coating, although not to the same extent as preferred Si/Cr ratios. Use in the above pack of 1.7 percent aluminum and 11.6 percent chromium will provide coatings with shorter service life due apparently to a nonlinearity in the relation of service life to aluminum over the range including 1.7 percent.

Control IV

The procedure of Example 2 is duplicated, but with quite low amounts of silicon in the pack composition such as might result from a silicon supply only from a silicide coating on an alloy part or from silicon associated as an impurity in one of the pack components. A diffusion coating containing between 1.5 and 2 per-

cent silicon by elemental analysis is obtained. Testing in the erosion rig shows localized etching and resultant premature failure, i.e., only a few hours per mil, typical of aluminum-chromium products containing no silicon.

The present invention is useful in the formation of various structures intended to be used in high temperature, highly corrosive environments. Thus, turbine engine parts such as nozzle guide vanes, blades or buckets, fuel nozzle covers, engine shrouds and valves for steam turbines are typical structures.

We claim:

1. Jet engine component or like structure having improved resistance to thermal fatigue cracking comprising a high temperature resistant base metal selected from cobalt, nickel and alloys in which cobalt or nickel is the largest single ingredient and a highly chemically resistant diffusion coating over at least a portion of the base metal and consisting essentially of 10 to 60 weight percent aluminum, 3 to 30 weight percent chromium, and from 0.6 to 1.4 parts by weight silicon per part of chromium but not less than 2.5 weight percent silicon, said coating being diffused into the base metal to a uniform depth of between 0.5 and 20 mils and between and across intergranular boundaries in the base metal.

2. Structure according to claim 1 in which intergranular spaces in the base metal beyond the uniform coating depth are free of aluminum introduced by the coating procedure.

3. Structure according to claim 1 in which said base metal is nickel.

4. Structure according to claim 1 in which said base metal is cobalt.

5. Structure according to claim 1 in which said base metal comprises nickel as the largest single ingredient.

6. Structure according to claim 1 in which said base metal comprises cobalt as the largest single ingredient.

7. Structure according to claim 1 in which said diffusion coating contains from 5 to 35 weight per cent silicon.

8. Structure according to claim 7 in which the crystalline arrangement of the diffusion coating layer is stable in air at 1,750°F.

9. Structure according to claim 1 in which said diffusion coating contains from 10 to 30 weight per cent aluminum.

10. The method of improving thermal fatigue cracking resistance in jet engine components or like structure comprising a high temperature resistant base metal selected from cobalt, nickel and alloys in which cobalt or nickel is the largest single ingredient which includes diffusing from 3 to 30 weight percent chromium and 10 to 30 weight percent aluminum into the structure surface at surface temperatures above about 1,750°C and for a time sufficient to form a diffusion coating from 0.5 mil to 20 mils in depth, and controlling the pattern of aluminum distribution through the diffusion coating to eliminate voids in the coating and intergranular incursions of aluminum into the base metal by incorporating silicon in the diffusion coating in an amount between 5 and 35 weight percent and in a ratio between 0.6 and 1.4 parts by weight of silicon per part of chromium.

11. Method according to claim 10 in which aluminum, chromium and silicon are sequentially diffused into the structure surface.

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12. Method according to claim 10 in which aluminum, chromium and silicon are simultaneously diffused into the structure surface.

13. Method according to claim 10 in which the structure surface is heated to not higher than 1,900°F during diffusion of the coating.

14. Method according to claim 10 in which the structure is immersed into a diffusion pack composition con-

taining 0.3 to 10 weight per cent aluminum, 3 to 40 weight per cent chromium and 5 to 35 weight per cent silicon for said diffusion.

15. Structure according to claim 1 in which said diffusion coating contains from 8 to 20 weight percent silicon.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,779,719 Dated December 18, 1973

Inventor(s) Eugene V. Clark, William J. Martin, Peter J. Plambeck
and Maurice R. Commanday

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 55; "face at surface temperatures above about 1,750°C and" should read --face at surface temperatures above about 1,750°F and--.

Signed and sealed this 10th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents