

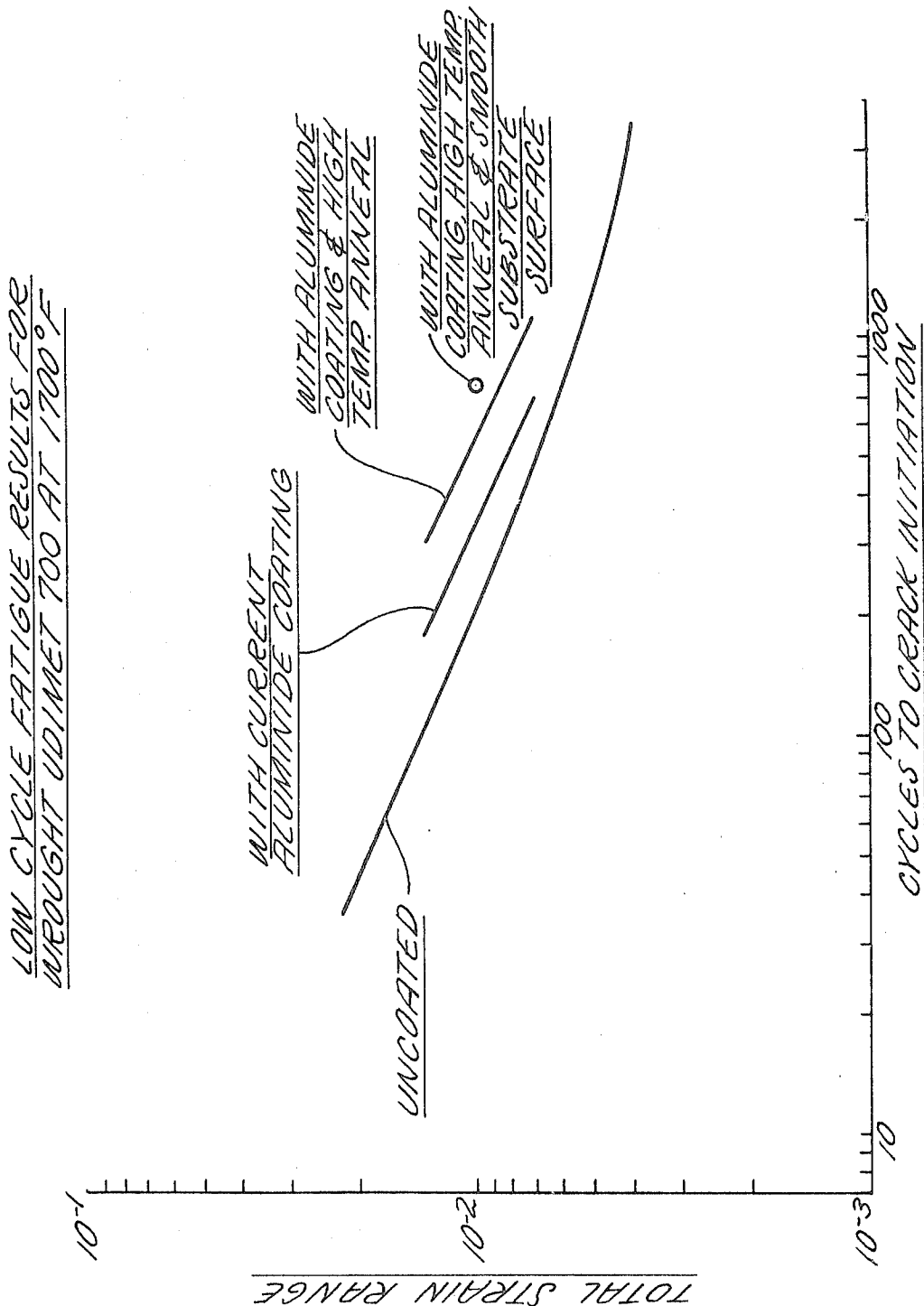
July 27, 1971

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3,595,712

PROCESSING OF ALUMINIDE-COATED NICKEL-BASE SUPERALLOYS

Filed Oct. 8, 1968



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## PROCESSING OF ALUMINIDE-COATED NICKEL-BASE SUPERALLOYS

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Filed Oct. 8, 1968, Ser. No. 765,777

Int. Cl. B23p 15/00; C21d 1/00

U.S. Cl. 148—162

8 Claims

### ABSTRACT OF THE DISCLOSURE

The fatigue properties of the aluminide-coated nickel-base superalloys, particularly in gas turbine engine applications, are improved by processing the coated article to decrease the brittleness of the coating, particularly through the use of a high temperature anneal between the coating and the substrate precipitation heat treatments. Concurrently, the overall coating process offers increased simplicity of processing with consequent economic advantages.

### BACKGROUND OF THE INVENTION

The present invention relates in general to the high-temperature, oxidation-resistant coatings, particularly the aluminide coatings as applied to the superalloys. It has specific utility in the processing of those coated gas turbine engine components formed from the nickel-base superalloys.

The achievements of higher strengths in the superalloy systems for gas turbine engine applications have generally been attained only at the expense of oxidation resistance. Accordingly, aluminide coatings were developed to permit exploitation of these alloys at temperatures higher than those possible with the alloys in an uncoated condition.

The aluminide coatings generally derive their protectivity from intermetallic compounds of aluminum which in turn are protected by a layer of aluminum oxide formed by high temperature oxidation of the coating. Gradually, the oxide is lost by a process of erosive spalling, but a reoxidation occurs and the protective function is reestablished. Accordingly, the substrate remains protected as long as sufficient aluminum is retained in the coating to provide the preferential oxidation mechanism leading to the formation of aluminum oxide. The protective character of the coating is, hence, a function of its aluminum content, the higher aluminum contents leading to improved component lifetimes in terms of oxidation behavior when viewed in the light of the progressive oxidation-erosion-reoxidation mechanism.

The typical aluminide coating may be formed in a number of ways, but the more widely used methods are those involving slurry-diffusion or pack cementation. In a typical slurry process utilizing a Udimet 700 substrate, a mixture of aluminum and silicon powders in a ratio of 9 to 1 is suspended in a cellulose acetate vehicle and applied by spray gun to the mechanically-abraded surface of a fully machined and heat treated article. After volatilization of the vehicle and reaction of the mixture with the substrate by exposure to an elevated temperature for a few minutes, the article is given the following heat treatment: diffusion at 1775° F. for 4 hours; plus 1550° F. for 24 hours; plus 1400° F. for 16 hours.

In a typical pack cementation process, the desired aluminide coating is generated by embedding the parts in a pack consisting of 15 percent aluminum powder, 3 percent ammonium chloride and 82 percent alumina and heating the pack to a temperature of perhaps 1800° F.

Both coating mechanisms proceed mainly by diffusion

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of aluminum into the substrate. Although the particular coating composition achieved reflects to some extent the structural and compositional characteristics of the substrate alloy, microstructural examination of a large number of contemporary coating-substrate systems indicates that most, if not all, aluminide coatings on the nickel-base superalloys are formed on and protect by similar mechanisms regardless of the method by which the coating is achieved.

Experience has shown that gas turbine engine components are frequently cycle limited, i.e., the fatigue properties are the fundamental factor in determining the useful life of the coated component. In most cases the fatigue failures are surface initiated and, hence, the surface characteristics must be tailored to provide optimum performance. Accordingly, the fatigue resistance of the coated component bears a direct relation to the properties of the coating. In the coated Udimet 700 system which is widely used in gas turbine blades under some circumstances the foremost factor influencing integrity is cyclic strain fatigue induced by engine acceleration and deceleration. Investigation of the isothermal low-cycle fatigue behavior at temperatures between 70° F. and 1700° F. has revealed that cracking does, in fact, invariably commence at an external surface or in the coating which is, of course, different in composition and structure than the substrate itself.

In this particular coating-substrate system, which is typical of the conventional aluminide-superalloy systems, the aluminide coating comprises a polycrystalline matrix of high aluminum content ( $\beta$  NiAl phase) together with a variety of interspersed second phases. This  $\beta$  aluminide phase having an aluminum content of typically 30-40 weight percent aluminum is characterized by very low ductility at temperatures below 1500° F. and, hence, is susceptible to crack formation. This low ductility is a function of the high aluminum content and results in a high brittle-ductile transition temperature usually within or above the designed component critical strain range.

Furthermore, as a necessary function of the coating operation, the substrate adjacent to the coating is altered in composition by withdrawal of species by the coating in a diffusion mechanism. In the case of the typical nickel-base superalloy, enrichment of cobalt and chromium occurs and subsequent heat treatment or engine operation results in the precipitation of an undesirable sigma ( $\sigma$ ) phase at the substrate surface.

### SUMMARY OF THE INVENTION

The primary object of the present invention is to improve the fatigue properties of aluminide coatings and coated articles, particularly in their application to the nickel-base superalloys and gas turbine engine components fabricated therefrom.

The foregoing object and other objects of the invention are achieved by altering the coating composition and/or structure particularly through the inducement of information of more optimum types, amounts and distribution of the various phases present in the coating and/or a minimization of the more detrimental phases by suitable processing. Contrary to the usual techniques, the processing is selected to reduce the localized aluminum content of the coating whereby, in addition to the reduction of brittle aluminide phases, and/or the formation of a ductile  $\text{Ni}_3\text{Al}$   $\gamma'$  phase grain boundary layer, there is an improved distribution of second phases in the structure. In a still further improvement, the substrate surface prior to coating is mechanically cleaned so as to furnish a surface roughness not exceeding about 65 microns/inch.

Briefly stated, the preferred processing contemplates an intermediate elevated temperature heat treatment between

the usual coating and substrate precipitation heat treatments, this intermediate heat treatment being conducted in the temperature range where the sigma or other detrimental phases are not stable.

This heat treatment results in an advantageous homogenization of the aluminide and the secondary phases in the coating and a reduction in the localized aluminum content of the coating. The particular temperature level selected for this intermediate heat treatment or high temperature anneal is both a function of the substrate composition and of the intended environment of the coated article and as such falls coincident with the substrate solutionizing temperature range. This provides a secondary advantage to the process in terms of economy for, in contradistinction to the conventional overall coating processes wherein coating is often effected on the fully heat treated article, the present process in terms of the overall cycle permits the achievement of improved coatings on articles in as-cast, as-wrought or as-machined condition, and the prior full heat treatments of the uncoated substrate may be conveniently eliminated.

The present process in an overall sequence hence involves coating of a substrate with or without prior full heat treatment thereof, usually but not necessarily including the usual short term heat treatment to set the coating; an intermediate high temperature anneal at the substrate solutionizing temperature; and a precipitation heat treatment cycle.

A particular preferred coating process for Udimet 700 components, including the intermediate high temperature anneal, thus becomes; coating, including on an optional basis, a diffusion heat treatment at 1975° F. for 4 hours; an intermediate heat treatment at 2140° F. for 4 hours; air cool plus 1975° F. for 4 hours—air cool plus 1550° F. for 24 hours; air cool plus 1400° F. for 16 hours; and air cool.

As applied to components formed of the MAR M200 alloy, the preferred processing becomes: coating, including on an optional basis, a diffusion heat treatment at 1975° F. for 4 hours; an intermediate heat treatment at 2200° F. for 2 hours; air cool plus 1600° F. for 32 hours; and air cool.

#### BRIEF DESCRIPTION OF THE DRAWING

The drawing is a graph depicting the results of low cycle fatigue testing of wrought Udimet 700 at 1700° F. with the sample in various conditions of processing.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

As used herein, the term nickel-base superalloys will be understood to have reference to those multiphase alloys of the  $\gamma$ - $\gamma'$  type characterized by high strengths in the temperature regimes of 1600°–2100° F. or higher. Some of the currently available alloys of this type are those listed below.

TABLE

Designation	Nominal composition (percent by wt.)
Udimet 700.....	15% Cr, 18.5% Co, 3.3% Ti, 4.3% Al, 5% Mo, .07% C, .08% B, balance Ni.
MAR-M200.....	9% Cr, 10% Co, 2% Ti, 5% Al, 12.5% W, 1% Co, .15% C, .015% B, .05% Zr, balance Ni.
IN-100.....	10% Cr, 15% Co, 4.5% Ti, 5.5% Al, 3% Mo, .17% C, .75% V, .015% B, .075% Zr, balance Ni.
TRW-1800.....	13% Cr, 9% W, 1.5% Co, .6% Ti, 6% Al, 0.07% B, 0.07 Zr, 0.09% C.
MAR-M246.....	9% Cr, 1.5% Ta, 10% Co, 2.5% Mo, 10.0% W, 1.5% Ti, 5.5% Al, 0.15% C, 0.10% Mn, 0.015% B, 0.05% Zr.

The various processes by which the aluminide coatings have been generated on the superalloys include pack cementation, hot dipping, slurry methods, vapor deposition, fused salt electrolysis, and flame or plasma spraying. Of these, the pack cementation and slurry methods appear to currently enjoy the widest utility. However, all of the described processes involve the reaction of aluminum or aluminum-rich materials with the surface regions of the substrate alloys at elevated temperatures, and the

aluminide coatings thus generated all depend for their protective effect upon the formation of an outer layer of aluminum oxide during exposure of the coating to a high temperature oxidizing environment. The specific composition of the coating and, to a lesser extent, the morphology of the secondary phases (carbides, etc.) vary somewhat as a function of substrate composition resulting from an interdiffusion of species in the coating process. However, the overall effect of these variations in microstructure and composition do not alter the basic principles involved in the coating and protective mechanisms.

It has been found that a change in the heat treatment of coated nickel-base superalloys leads to a significant increase in their low-cycle fatigue crack initiation resistance which, as previously mentioned, is an important limiting factor for coated gas turbine engine components in terms of their useful lifetimes. The new processing is primarily directed toward decreasing the localized aluminum content of the coating. With the typical conventional coating techniques localized aluminum contents of 30–40 percent are typical while in the instant case the range is typically 20–25 percent. In a sense, therefore, the aluminum content of the coating is decreased. This is true, however, only in a localized sense for in reality there is about the same volume of aluminum present in the coating achieved by the present processing but it is subject to an improved distribution in the coating.

With a decrease in the localized aluminum content of the coating and the consequent preferred formation of a small but significant quantity of the more ductile  $\text{Ni}_3\text{Al}\gamma'$  aluminide phase surrounding the brittle  $\beta$  phase, there is also achieved a consonant change in grain size and morphology in the coating. The structure is homogenized; fine secondary phases are taken into solution; and the grain size is coarsened. Further, the preferred processing eliminates or at least substantially minimizes the substrate alloy segregation which is evident on metallographic examination of conventionally coated specimens. Concurrently, the brittle-ductile transition temperature for the improved coating is lowered to a less critical temperature range.

All of the above advantages resultant from the present invention are achieved primarily by a revision in the heat treatments applied to the coated component. It was found that the low-cycle fatigue crack resistance of coated Udimet 700 components could be significantly increased solely by heat treatment. In this particular system, a high temperature anneal at 2140° F. for 4 hours between coating and the substrate precipitation heat treatments was found to provide a dramatic improvement in coating ductility. The overall processing cycle for Udimet 700 thus becomes: coating of the alloy including optionally a diffusional heat treatment at 1975° F. for 4 hours; a high temperature anneal at 2140° F. for 4 hours; plus heat treatments at 1975° F. for 4 hours, 1550° F. for 24 hours and 1400° F. for 16 hours.

In the past, the coatings have as a matter of practice been applied to the fully heat treated blade or vane. This, of course, has involved a prior component heat treatment cycle prior to coating. In accordance with the present invention, through utilization of a high temperature anneal after coating, it is now possible to heat treat the coating and substrate simultaneously and, accordingly, the prior substrate heat treatments may be eliminated. In other words, coating may be effected on the blades and vanes as-wrought, as-machined or as-cast. Not only is the fatigue behavior of the coating improved but the overall processing cycle is considerably simplified with the consequent considerable cost savings in generation of the coated article. In actual practice with the new processing, it is possible as a general rule to eliminate the diffusional heat treatment usually associated with the actual coating cycle since the high temperature anneal will in itself serve to set the coating and provide the requisite diffusional mechanism desired.

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The temperatures, times and sequences described above are, of course, only representative as those skilled in the art will readily recognize. These parameters will vary from alloy to alloy and are primarily a function of substrate composition, although other factors such as intended usage are frequently considered. In particular, the time at temperature is generally susceptible to the greatest latitude in terms of specificity and is, within the bounds of reasonable interpretation, the least critical element involved. The intermediate heat treatment between coating and the substrate precipitation heat treatments, or high temperature anneal, will be conducted at a temperature generally consonant with the substrate solutionizing temperature. Representative solutionizing temperatures for a number of the nickel-base superalloys are set forth in the following table.

TABLE II

Designation:	Normal solutionizing temp., ° F.
Udimet 700	2100-2150
MAR-M200	2200-2230
IN-100	2150
MAR-M246	2200-2250
TRW 1800	2200-2250
Nimonic 115	2175
Udimet 710	2150
Rene 41	2150
TRW 1900	2200-2250

Briefly stated the overall processing sequence comprises coating the substrate; annealing the coated substrate at about the substrate solutionizing temperature; and precipitation heat treating the coated article.

As clearly indicated in the drawing, adherence to the above procedure results in improved crack initiation resistance and consequently fatigue resistance at 1700° F. The improvement in performance over the conventionally coated hardware is about a factor of 3 at 1400° F. and a factor of about 2 at 1700° F. And the yield stress of the coated component is virtually unaffected by the change in procedure.

The majority of the experimental specimens were tested at about 1500° F. in low cycle reverse bending fatigue at a total strain range of 1 percent utilizing substrates of various thickness. Coating thicknesses were generally 0.002-0.005 inches to correspond with the usual thickness range employed in the protection of gas turbine blades and vanes. A summarized comparative evaluation of such specimens is set forth in Table III.

TABLE III

Substrate thickness (in.)	Cycles to cracking	
	Conventional processing	New processing
.080	1,148	2,950
.080	1,154	
.040	538	
.040	680	1,836

As additionally indicated in the drawing if, prior to coating, the substrate surface is processed to achieve a surface roughness less than about 65 microns/inch, a smoother coating results and further improvement in fatigue crack initiation resistance is attained.

From the foregoing description, it will be seen that through the improved processing of this invention there has been provided means for doubling or tripling the useful lifetimes of coated superalloy components. Furthermore, the results are attained synergistically for, not only is the primary objective of this invention provided, there is also provided means by which the overall cost of fabricating coated superalloy components may be reduced.

While for the sake of clarity, the present invention has been described in connection with certain preferred em-

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bodiments and examples, these are intended to be illustrative only and no limitation is intended thereby. The invention in its true spirit and scope is set forth in the appended claims.

We claim:

1. In those processes wherein an aluminide coating is formed on a nickel-base superalloy substrate by diffusion of aluminum therein, the improvement which comprises: between the steps of applying the coating and precipitation heat treating the coated substrate, annealing the coating at above about 2100° F. so as to effectuate a solutionizing of the substrate.

2. The improvement according to claim 1 wherein: the annealing is conducted to reduce the localized aluminum content of the coating and to promote the formation of the ductile  $Ni_3Al\gamma'$  phase of the aluminide in the coating.

3. The improvement according to claim 2 wherein: the localized aluminum content is reduced to a maximum of about 25 percent by weight.

4. The improvement according to claim 1 in which: the surface roughness of the superalloy substrate prior to coating is held to a maximum of about 65 microns per inch.

5. The process for forming an aluminide coating on a nickel-base superalloy substrate which comprises the steps of, in sequence:

aluminizing the substrate surface;

heat treating the aluminized substrate at about 2100° F. for solutionizing the substrate;

and precipitation heat treating the substrate.

6. The process for forming an aluminide coating on a nickel-base superalloy gas turbine article which comprises the steps of, in sequence:

aluminizing at least a portion of the surface of the article;

heat treating the article at about the substrate solutionizing temperature to solutionize the substrate and effect a reduction in the localized aluminum content of the coating and promote the formation of the  $Ni_3Al\gamma'$  phase of the aluminide at the grain boundaries; and precipitation heat treating the article.

7. The process according to claim 6 wherein:

the surface of the article to be aluminized is provided with a surface roughness not exceeding about 65 microns per inch.

8. The process according to claim 7 wherein:

the intermediate heat treatment is conducted to provide a localized aluminum content in the coating less than about 25 percent by weight.

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29-197; 117-22, 107.2, 131; 148-31.5