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D. H. MAXWELL

3,573,963

METHOD OF COATING NICKEL BASE ALLOYS WITH A MIXTURE
OF TUNGSTEN AND ALUMINUM POWDERS

Original Filed July 5, 1966

2 Sheets-Sheet 1

FIG. 1

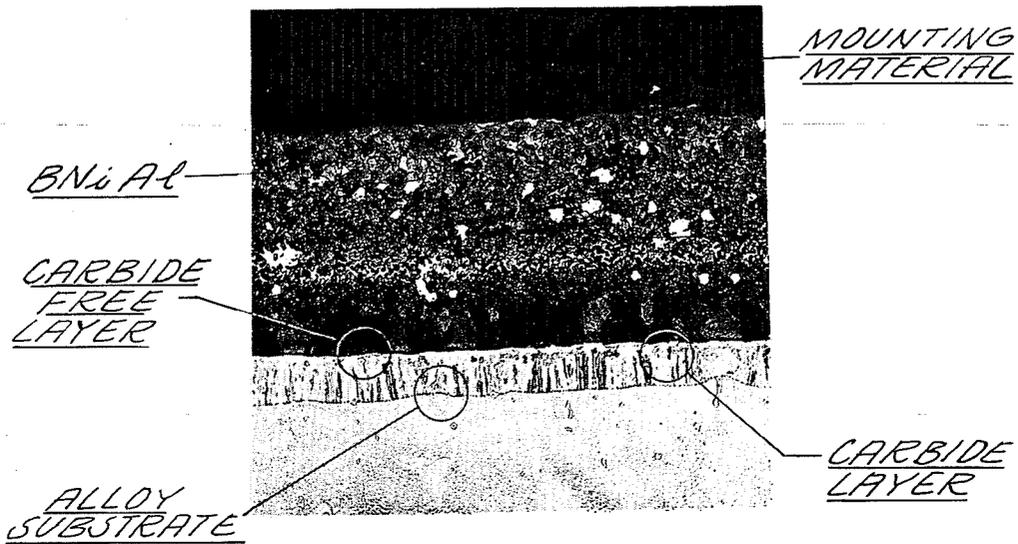
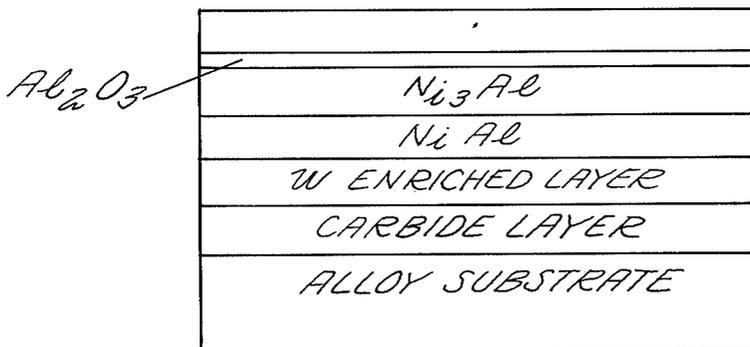


FIG. 2



INVENTOR
DOUGLAS H. MAXWELL
BY *Richard N. James*
ATTORNEY

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D. H. MAXWELL

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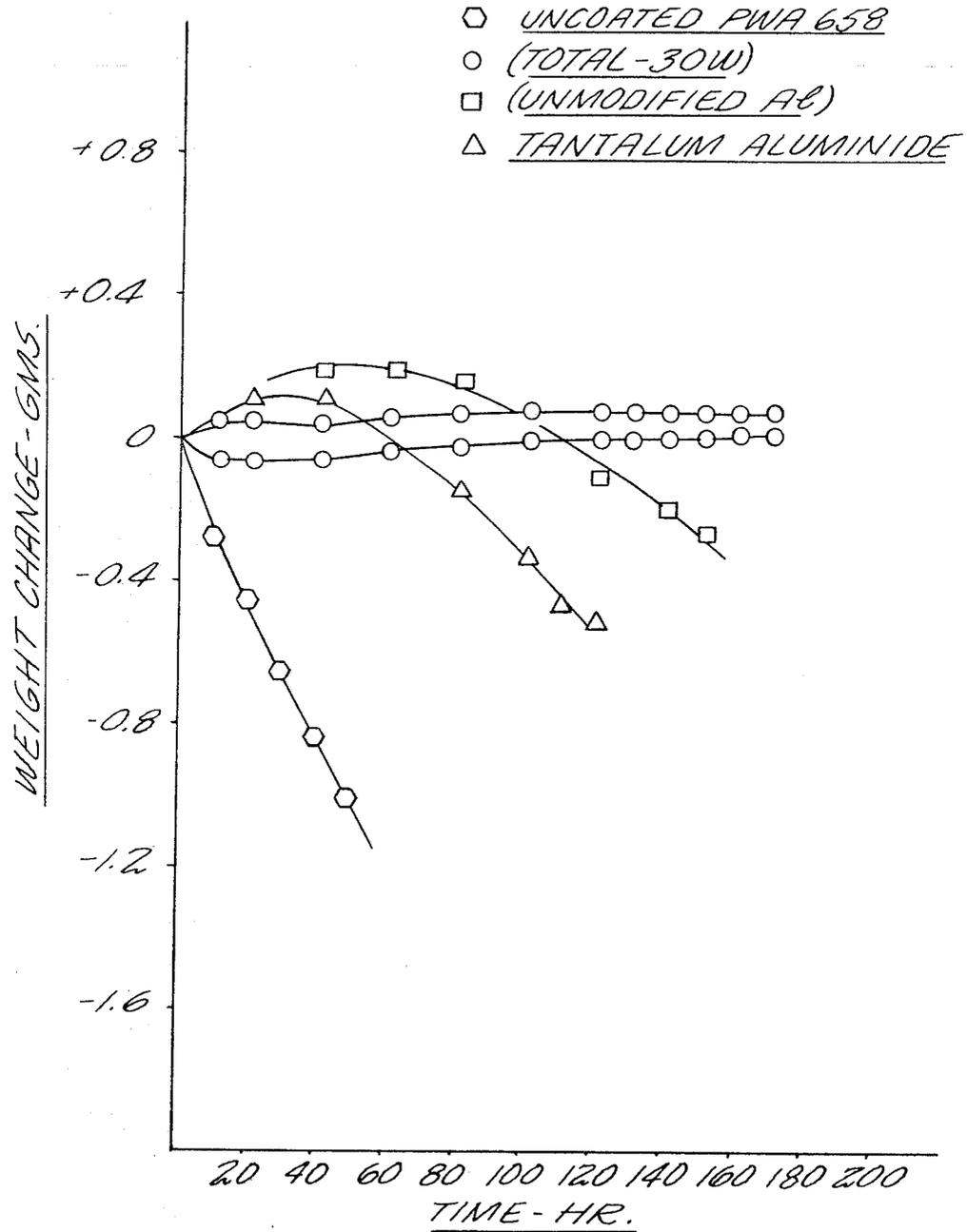
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FIG. 3

OXIDATION-EROSION TESTING OF COATED
PWA 658 AT 2100°F



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METHOD OF COATING NICKEL BASE ALLOYS WITH A MIXTURE OF TUNGSTEN AND ALUMINUM POWDERS

Douglas H. Maxwell, North Palm Beach, Fla., assignor to United Aircraft Corporation, East Hartford, Conn.

Original application July 5, 1966, Ser. No. 562,648, now Patent No. 3,450,512, dated June 17, 1969. Divided and this application Dec. 20, 1968, Ser. No. 810,876

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U.S. Cl. 117-71

10 Claims

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ABSTRACT OF THE DISCLOSURE

High temperature nickel base alloys are metallized with a mixture of powders consisting of 60-90 weight percent aluminum and 10-40 weight percent tungsten. The coated alloys are subjected to a diffusion heat treatment to form a tungsten-modified, aluminum-rich intermetallic.

Dispersion strengthened nickel base alloys are coated with a layer of nickel and subjected to a diffusion heat treatment prior to application of the aluminum-tungsten mixture.

This is a division of application Ser. No. 562,648, filed July 5, 1966 and now U.S. Pat. 3,450,512 issued June 17, 1969.

This invention relates in general to coated aircraft engine parts fabricated from the high temperature nickel base alloys and methods of producing the same. It contemplates the provision of a protective coating on these parts, not only to improve their oxidation erosion resistance at engine operating temperatures in excess of 2000° F., but also to improve their thermal shock resistance and creep rupture strength, by substantially reducing the interdiffusion between the base metal and the coating material.

According to the present invention, the heat affected engine parts are provided with a coating comprising a mixture of powders consisting essentially of, by weight, 60-90% aluminum and 10-40% tungsten in a hot spraying operation. After an appropriate diffusion heat treatment, a hard, oxidation-resistant barrier is formed on the engine parts through the establishment of a tungsten-modified, aluminum-rich intermetallic, by means of which the operating lifetime of the parts are greatly extended without sacrificing the advantageous mechanical properties inherent in the nickel base alloys. The presence of substantial amounts of tungsten in solid solution in the finished coating provides an effective interdiffusion barrier by means of which migration of aluminum into the base metal and diffusion of nickel to the surface of the coating is very significantly reduced.

A variety of high temperature nickel base alloys enjoy wide utility in the gas turbine engine industry because of their excellent mechanical properties under load in the high temperature environments associated with the operation of these engines. As a general rule, however, they do not display sufficient inherent oxidation resistance to permit engine operation lives and time between overhaul of reasonable duration, unless they are afforded appropriate surface protection. Accordingly, it has been the practice, even at the lower engine operating temperatures, to utilize coatings of various types on the nickel base alloy elements which are exposed to the hot, erosive engine gases.

Numerous coatings have been proposed and utilized in the industry to provide the desired protection, illustrative coatings of this nature being described in the patents to Hanink et al., 3,129,069 and Joseph, 3,102,044. These coatings were conceived and developed in an era

when, as a general rule, engine operating temperatures were confined to a hot section temperature maximum of 1900° F. It has always been desirable and, more recently, has become necessary, from the standpoint of engine economy, efficiency and performance to increase the engine operating parameters as a result of which sustained operating temperatures approximating 2100° F. are now prescribed. And in this operating range, the prior art coatings and techniques are no longer satisfactory.

As hereinbefore indicated, the previous methods for affording oxidation resistance to the nickel base alloys were generally confined to applications wherein exposure was limited to temperatures on the order of 1900° F., except perhaps for incidental, temporary engine excursions beyond that limit. At a temperature of approximately 2000° F., nickel and the nickel base alloys begin to exhibit a great alloying affinity for most of the usual coating materials, and particularly aluminum. As a result, the nickel acts as a sink for the aluminum coating, leading to a rapid depletion of aluminum at the exposed surface of the article and consequent contamination of the base metal.

It is evident that, as a result of interdiffusion between the coating and base metal, deterioration of the properties of the coated alloy occurs in two ways. First, as the coating material migrates into the base metal, its composition is altered with the usual result that the physical properties of the alloy obtained from its initial formulation are seriously diminished. Engine tests have revealed, for example, that unmodified aluminum coatings on nickel alloy first stage turbine blades have completely diffused through the thin trailing edge section of the blades in periods as short as 20 hours, leading to premature blade failure at the trailing edge. The problem is so severe that, as an interim solution, it has been found preferable to leave the blades uncoated in this area rather than to suffer the strength loss incident to the base metal contamination. Secondly, in the interdiffusion mechanism, aluminum is rapidly depleted from the surface of the article and replaced by other alloy components which do not necessarily display satisfactory oxidation erosion resistance and hence, the protective function of the coating is soon lost and oxidation erosion is once more evident on exposure to the engine gases. Furthermore, the other surface oriented physical properties such as thermal shock resistance and creep rupture strength are significantly reduced.

It is a principal object of the present invention to provide coated nickel alloy engine parts which will withstand higher engine operating temperatures than those currently in use, with no sacrifice of either the oxidation erosion resistance of the parts or of the mechanical properties of the base metal.

A further object of the invention is to provide an improved coating for the nickel base alloys wherein the interdiffusion between the base metal and the coating materials is substantially reduced and the coating is thus made applicable to those engine parts designed to operate at sustained temperatures in excess of 2000° F.

Another object is to provide aircraft engine parts suitable for use in high temperature oxidizing environments through the establishment of a surface coating on the parts consisting essentially of a tungsten-modified aluminum-rich alloy in combination with the various elements comprising the base metal.

An additional object is to provide methods for imparting inter-diffusion resistance to the coated nickel base alloys.

These and other objects and advantages of the present invention will be set forth in the following detailed description of the invention or will be evident therefrom or from practice of the invention.

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In order to more clearly describe the instant invention and more particularly point out its principal advantages, reference will be made in the following description to the attached drawings of which:

FIG. 1 is a photomicrograph of the present coating on a nickel base alloy prior to exposure of the alloy at high temperature to an oxidizing environment. Magnification is 1,000 \times .

FIG. 2 is a somewhat simplified schematic representation of the coating after exposure to temperatures of 2100° F. in an oxidizing atmosphere.

FIG. 3 is a graph illustrating the comparative results of oxidation erosion testing at 2100° F. of coated turbine blades according to this invention as related to both coated and uncoated reference parts.

To provide the protective surface layer on the nickel base alloys and, hence, the desired oxidation-erosion and thermal shock resistance, the following preferred process is recommended.

The surfaces to be coated are thoroughly preconditioned to provide a suitable surface to which the coating may metallurgically bond. Blasting with No. 60 aluminum oxide grit is used to remove the gross surface impurities. The grit blasting is followed by a thorough surface cleaning to eliminate all dirt, grit, oil, grease, stains and other residual foreign matter. A power flush with water, air drying or air blasting with oil and water-free air, and an acetone rinse have been found effective in this regard. In some instances, a simple degreasing will be sufficient, while in other cases it may be found advantageous to utilize acid or caustic pickling baths. In any event, however, the foregoing preconditioning operation will provide a contaminant free surface to which the coating material may be applied and to which the coating will bond uniformly.

Following the cleaning phase, a thoroughly blended mixture of powders consisting essentially of, from (60-90) weight percent aluminum, and (10-40) weight percent tungsten, or, more preferably, (68-72) weight percent aluminum and 28-32 weight percent tungsten, is uniformly deposited onto the designated surfaces to a depth of 0.004-0.005 inch. Because of the wide diversity of melting points, the deposition will normally be effected in a metallizing operation, the term "metallizing" having reference to the application of materials by hot spraying techniques.

Blending of the powders will normally be performed immediately prior to the metallizing operation to prevent separation of the powders in the container because of size and density differences. Since the protective function of the coating is to a great extent dependent upon the uniform dispersion of tungsten throughout, as hereinafter discussed in greater detail, any premature stratification of powders in the hopper feeding the spray torch will reduce the efficacy of the technique.

In essence the metallizing process is conducted as though powdered aluminum alone is being utilized and the hot spraying parameters are adjusted accordingly. Gas pressures of 10 p.s.i. acetylene, 15 p.s.i. oxygen, and 60 p.s.i. air in a Wall Colmonoy Model C-2 Power Metal Spray Gun or equivalent are satisfactory.

While, in general, it may be said that, the finer the particles the more uniform the coating, it is generally preferable to maintain the powder size of the aluminum between -100 and +325 mesh (43-147 microns), the mesh sizes reported being Tyler Standard. As a practical matter, if the particle size of the aluminum is too fine, excess oxide present as a thin layer on each particle, may be introduced into the coating and the presence of this oxide in excessive amounts will interfere with the subsequent interaction between components which is desired and effected during subsequent heat treatment steps. On the other hand, as above indicated, it is usually preferable to maintain the powder sizes as fine as possi-

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ble, consistent with the hereinbefore mentioned oxide inclusion, to promote uniformity of the coating.

The tungsten, which is present in the powder mixture in a preferred amount of about 30 weight percent, preferably has a particle size of from 1-5 microns. Its particle size is held small to facilitate a later alloying reaction which is effected between the coating material and the base metal at which time the tungsten goes into solid solution. Another reason for maintaining a small particle size on the part of the tungsten will be evident by reference to the wide diversity of melting points between the aluminum and the tungsten. At the spraying parameters used for aluminum, tungsten is not melted and it is, accordingly, necessary for the aluminum to act as a carrier for the tungsten whereby it is dispersed uniformly by entrapment within the aluminum on the surface to be coated.

From the practical viewpoint, it will be noted that hot spraying techniques will generally be the preferred method of applying the raw coating to the surface to be protected. However, it will similarly be seen that, as far as the protective function of the coating is concerned and particularly as related to its interdiffusion resistance, the method of application appears to be relatively immaterial as long as the surface is provided with a uniform dispersion of tungsten in aluminum within the weight ranges discussed.

The deposition of the raw coating onto the surface to be protected to a thickness of 0.004-0.005 inch has proved satisfactory in most cases involving use of this process on gas turbine engine parts. It will be noted, however, that generally this depth of coating is somewhat greater than that usually preferred by other processes for the same environment and endurance, except insofar as temperature exposure is concerned. But the particular thickness applied is not necessarily critical. It will be evident that a sufficient depth of coating must be provided to maintain the oxidation barrier for the length of service expected for the part, since in actual use there is a gradual oxidation and erosion thereof during its lifetime. On the other hand, it is generally advantageous to limit the thickness of the coating to the minimum amount necessary for the protective function, with an appropriate safety factor. The coating material necessarily imposes a weight penalty on the system wherein it is used and, although the thickness is small, it may be applied to many parts and the cumulative weight effect may be substantial.

Subsequent to metallizing operation, the coated parts are diffusion heat treated to form a nickel-aluminum alloy, nickel-aluminide (NiAl) at the surface of the article; distribute the tungsten in solid solution; and metallurgically bond the coating to the substrate. In the case of the nickel base alloys, the diffusion heat treatment will be conducted at a temperature between 1950° F. and the melting point of the base metal in a non-contaminating atmosphere, including hydrogen, inert gas or vacuum, for a period of time sufficient to form the aluminum-nickel alloy. The most preferred heat treatment will be conducted at a temperature of from 1950-2000° F. in a hydrogen atmosphere for 4 hours.

Following the heat treatment, the age-hardenable alloys are usually cooled to below 900° F. within 23 minutes or less in hydrogen or other noncontaminating atmosphere. After cooling to room temperature, any loose oxide film resultant from the heat treatment is removed by power flushing with water.

Parts coated by the above-described method were subjected to extensive analysis and testing and a variety of nickel base alloys were utilized.

One of the more outstanding alloys tested comprises the following composition, by weight, (0.15-0.2) % carbon, (8-11) % chromium, (13-17) % cobalt, (2-4) % molybdenum, (4.5-5) % titanium, (5-6) % aluminum, (10-11) % aluminum + titanium, (0.7-1.2) % vanadium,

(0.01–0.02)% boron, (0.03–0.09)% zirconium, balance nickel, and is hereinafter identified as PWA 658. Turbine blades fabricated from the PWA 658 alloy were prepared in accordance with the teachings described herein and compared with similar blades coated by the prior art methods.

The comparative effects of the stress rupture testing is detailed in Table I.

TABLE I

System	Test conditions (temp., ° F./p.s.i.)	Life (hours)	Percent elonga- tion	Percent reduction in area
Unmodified Al (Group A)-----	1,800/26,700	50.7	12.4	23.9
	1,900/14,700	103.2	18.8	21.9
	2,000/9,220	65.2	10.2	14.6
	2,100/5,060	25.9	16.2	15.9
	2,100/5,060	18.6	10.6	14.6
70Al-30W (Group B)-----	1,800/26,700	43.9	4.8	4.5
	1,800/26,700	63.4	9.2	16.3
	1,900/14,700	116.3	12.1	24.2
	1,900/14,700	95.2	9.4	8.9
	2,000/9,220	62.4	7.7	10.0
	2,000/9,220	51.5	11.9	22.5
	2,100/5,060	52.0	14.9	15.3
	2,100/5,060	55.4	12.9	9.9

It will be seen from the results enumerated in Table I, that the time to rupture of the specimens is roughly the same with the two coatings up to a temperature of 2000° F. However, at 2100° F., the time to rupture of the specimens carrying the (70Al-30W) coating (Group B) was over twice that of the specimens carrying the prior art coating (Group A).

Melting was observed on the Group A blades between 2150° and 2200° F., while melting of the Group B blades occurred at 2200°–2250° F., or approximately 50° F. higher in the case of the Group B blades. Oxidation-erosion testing of the Group A specimens revealed spotty coating failure in 40–60 hours whereas the Group B samples revealed no coating failure at least to 150 hours.

In terms of diffusional stability, the Group B specimens again proved far superior to the specimens coated by the prior art methods. On exposure for 120 hours at 2100° F. in static air, the Group A blades showed a 250 percent increase in coating thickness while under the same exposure the Group B material illustrated a 40 percent increase, indicating that the tungsten addition is very instrumental in reducing the coating/base metal interdiffusion. Of perhaps even greater significance is the fact that the Group B specimens showed very little coating alloy depletion whereas the Group A samples displayed total depletion.

Approximately 100 blades were subjected to actual engine operation on JP-5 turbine fuel at 2100° F. for a total of over 400 hours. The results of these tests are summarized in FIG. 3. The excellent stability and superiority of the (70Al-30W) coating in an actual engine operating environment was dramatically illustrated in these tests.

Similar excellent results were obtained with the nickel base alloys analyzing as follows, by weight, (0.08–0.13)% carbon, (7.5–8.5)% chromium, (9.5–10.5)% cobalt, (5.75–6.25)% molybdenum, (5.75–6.25)% aluminum, (4–4.5)% tantalum, (0.8–1.2)% titanium, (0.01–0.02)% boron, (0.05–0.1)% zirconium, balance nickel.

In tests conducted in connection with the dispersion strengthened nickel base alloys, referred to in the trade as TD Nickel, analyzing at, by weight, (1.80–2.60) thoria, balance nickel, the advantages of the tungsten modified aluminum coating were similarly evident. In connection with the TD Nickel, however, it was found necessary to metallize the surfaces to be coated with a layer of nickel and subsequently diffusion heat treat the alloy, prior to the application of the (70Al-30W) coating. TD Nickel is notoriously difficult to provide with a satisfactory coating of long endurance. The coating/base metal interdiffusion problem previously discussed appears to be particularly troublesome in the case of these alloys. Furthermore, the surface sites of the thoria appear to nucleate porosity in the

applied coatings whereby both the protective effect and the adherence of the coating are adversely affected in a very short period of time.

In the case of the TD Nickel parts, therefore, nickel powder is applied by plasma spraying techniques to the surface to be protected to a depth of preferably 0.005–0.007 inch. Subsequent to the plasma spraying the part is subjected to a diffusion heat treatment at 2175–2275° F.

for about four hours in a non-contaminating atmosphere such as hydrogen. It is only after this initial surface preparation that the (70Al-30W) coating is applied. The basic oxidation erosion protection, however, stems from the tungsten-modified aluminum rich layer as hereinbefore described.

The coating, as applied and before heat treatment, consists essentially of aluminum with entrapped tungsten particles uniformly dispersed throughout. Following the diffusional heat treatment, and as best seen in the photomicrograph identified as FIG. 1, a hard, ductile surface layer of beta nickel-aluminide is formed. The beta aluminide has a melting point on the order of 3200° F. and a Rockwell hardness of Rc 45–50. Microprobe analysis also indicates that the presence of substantial amounts of tungsten and other elements included in the base metal composition, however, for the purposes of this discussion, particularly insofar as the oxidation erosion mechanism is concerned, it will be referred to as nickel aluminide. The bulk of the tungsten, however, and other refractory metals appears to be concentrated in the area between the exterior surface of the coating and a carbide layer which forms on the surface of the base metal. The presence of this tungsten in solid solution between the surface layer and the base metal operates as an effective diffusion barrier, the tungsten itself having an extremely slow diffusion rate into the nickel.

Experimentation has revealed that amounts of tungsten less than about ten weight percent do not provide sufficient material in the interdiffusion barrier to be effective to the extent desired. On the other hand, amounts greater than about 40 weight percent lead to excessive quantities of tungsten in the surface layer, tungsten being readily oxidizable at the engine operating temperatures involved and prone to the formation of brittle compounds, neither condition being tolerable.

The necessity for limiting the amount of tungsten in the coating should similarly be considered in selection of the nickel base alloy and composition of the mixture of powders applied thereto. Articles coated by the foregoing techniques were prepared from an alloy consisting of, by weight, (0.12–0.17%) carbon, (8–10%) chromium, (9–11%) cobalt, (11.5–13.5%) tungsten, (0.75–1.25%) columbium, (1.75–2.25%) titanium, (4.75–5.25%) aluminum, (0.01–0.02%) boron, (0.03–0.08%) zirconium, balance nickel. The results achieved with these articles with respect to their oxidation erosion resistance were not as satisfactory as those achieved with the other nickel base alloys. It is postulated that the presence of significant amounts of tungsten in the base metal contributed to the deterioration of properties. The interplay between the tungsten in the coating as applied and that present in the

base metal, and the necessity for careful consideration thereof, was thus clearly demonstrated.

Upon exposure at temperature to an oxidizing environment the nickel aluminide is oxidized, and the oxidation is preferential whereby virtually one hundred percent aluminum oxide is formed, the aluminum oxide gradually being lost by an erosion process. However, oxide penetration of the coating does not take place during the designed lifetime of the part and as long as the coating remains intact and, in a sense, preferentially oxidizable. The schematic of FIG. 2 illustrates the postulated mechanism involved in the oxidation erosion problem.

As the oxidation erosion process continues, aluminum combining with oxygen and gradually being lost by erosion, the excess nickel promotes the formation of nickel aluminide in another form, Ni_3Al , immediately beneath the surface layer of oxide.

It will be evident from reference to the graph in FIG. 3 that the oxidation-erosion with the coated engine parts of the present invention proceeds very slowly with no significant weight loss being evident for a period exceeding 150 hours. When compared to the currently available coatings in the same environment its advantages thereover are manifest.

Other modifications to the coating and process will be evident to those skilled in the art within the true spirit of the present invention. The ability of tungsten in solid solution to operate as a diffusion barrier for the nickel base alloys will have broader application than utility with pure aluminum. Furthermore, at the sacrifice of some deterioration in the properties of the coated article, it is possible to substitute molybdenum for some of the tungsten in the material as applied, molybdenum also offering a considerable degree of interdiffusion resistance to the nickel base alloys, albeit not to the same degree as tungsten. Accordingly, while the present invention has been described in particular detail with particular reference to certain examples and preferred embodiments, the true scope and spirit of the invention will be understood to be as set forth in the appended claims.

What is claimed is:

1. The method of imparting oxidation erosion resistance at temperatures above 2000° F. to the high temperature nickel base alloys comprising the steps of:

metallizing the surface of the alloys with a mixture of powders consisting essentially of, by weight, (60-90%) aluminum and (10-40%) tungsten, and diffusion heat treating the metallized alloy in a non-contaminating atmosphere at a temperature sufficient to effect an alloying reaction of the mixture with the alloy substrate.

2. The method of claim 1 wherein the diffusion heat treatment is conducted at a temperature of at least 1950° F.

3. The method of claim 2 wherein the mixture of powders consists essentially of, by weight, (68-72%) aluminum, balance tungsten.

4. The method of imparting oxidation erosion resistance at temperatures above 2000° F. to the high temperature dispersion strengthened nickel base alloys comprising the steps of:

coating the surface of the alloy with a layer of nickel, diffusion heat treating the nickel coated alloy in a non-contaminating atmosphere, metallizing the surface of the alloy with a mixture of powders consisting essentially of, by weight, (60-90%) aluminum and (10-40%) tungsten, and diffusion heat treating the metallized alloy in a non-contaminating atmosphere at a temperature sufficient to effect an alloying reaction of the mixture with the alloy substrate.

5. The method of claim 4 wherein the first heat treat-

ment is conducted at a temperature of at least 2175° F. and the second heat treatment is conducted at a temperature of at least 1950° F.

6. The method of claim 5 wherein the nickel base alloy consists essentially of, by weight, (1.8-2.6)% thoria, balance nickel.

7. The method of claim 6 wherein the mixture of powders consists essentially of, by weight, (68-72)% aluminum, balance tungsten.

8. The method of imparting oxidation erosion resistance at temperatures above 2000° F. to the high temperature nickel base alloys comprising the steps of:

blending a mixture of fine powders consisting essentially of, by weight, (68-72)% aluminum and (28-32)% tungsten, the aluminum having a particle size of about (43-147) microns and the tungsten having a particle size of about (1-5) microns,

applying the mixture by means of a flame spray to the surface to be protected to a thickness of at least 0.004 inch,

and diffusion heat treating the coated alloy at a temperature of 1950-2000° F. for a period of approximately 4 hours in a non-contaminating atmosphere.

9. The method of imparting oxidation erosion resistance at temperatures above 2000° F. to the thoria dispersed nickel base alloys comprising the steps of:

plasma spraying the surfaces to be protected with nickel powder to a thickness of at least 0.005 inch,

diffusion heat treating the nickel coated alloy at 2175-2275° F. for about 4 hours in a non-contaminating atmosphere,

providing a thoroughly blended mixture of powders consisting essentially of, by weight, (68-72)% aluminum and (28-32)% tungsten, the aluminum having a particle size of about (43-147) microns and the tungsten having a particle size of about (1-5) microns,

applying the mixture by means of a flame spray to the surface to be coated to a thickness of at least 0.004 inch,

and diffusion heat treating the coated alloy at a temperature of 1950-2000° F. in a non-contaminating atmosphere for a period of approximately 4 hours.

10. In the processes for imparting oxidation resistance to the high temperature nickel base alloys wherein an aluminum rich intermetallic is formed as a surface layer thereon, the improvement which comprises providing a tungsten enriched intermediate layer between the surface layer and the alloy substrate, the tungsten being present in solid solution in an amount of about (10-40) weight percent.

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ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, JR., Assistant Examiner

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