

Sept. 19, 1961

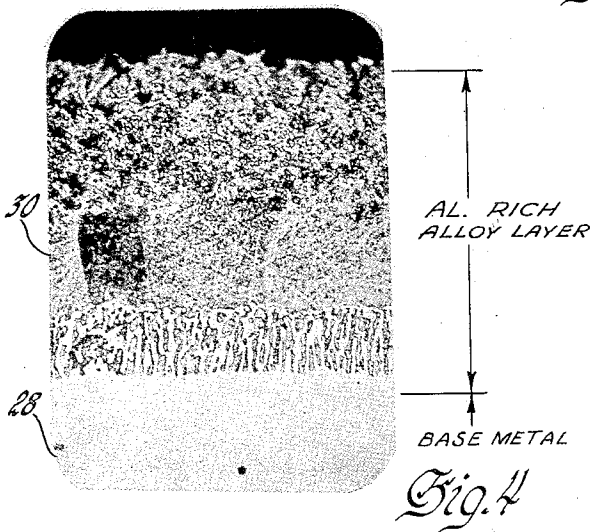
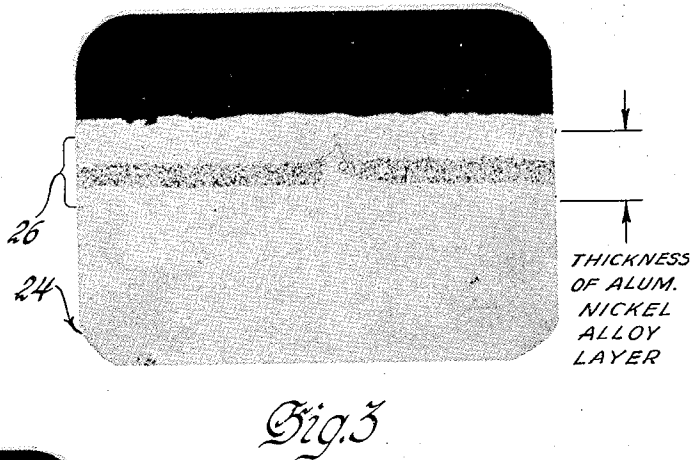
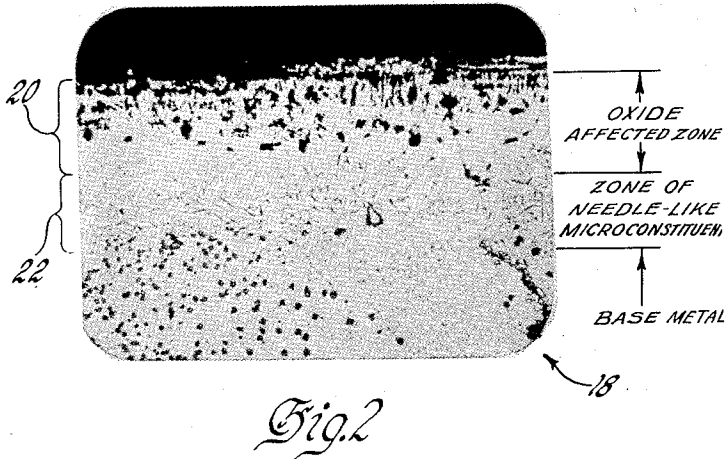
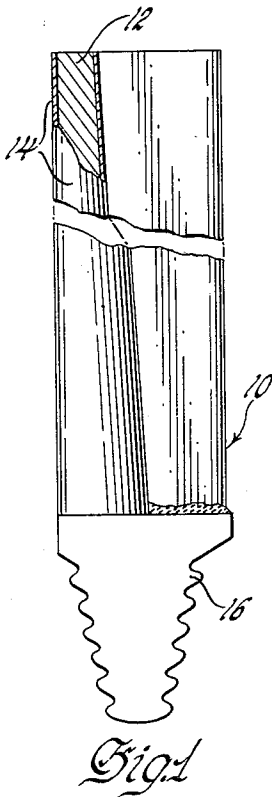
D. K. HANINK ET AL

3,000,755

OXIDATION-RESISTANT TURBINE BLADES

Filed Oct. 11, 1956

3 Sheets-Sheet 1



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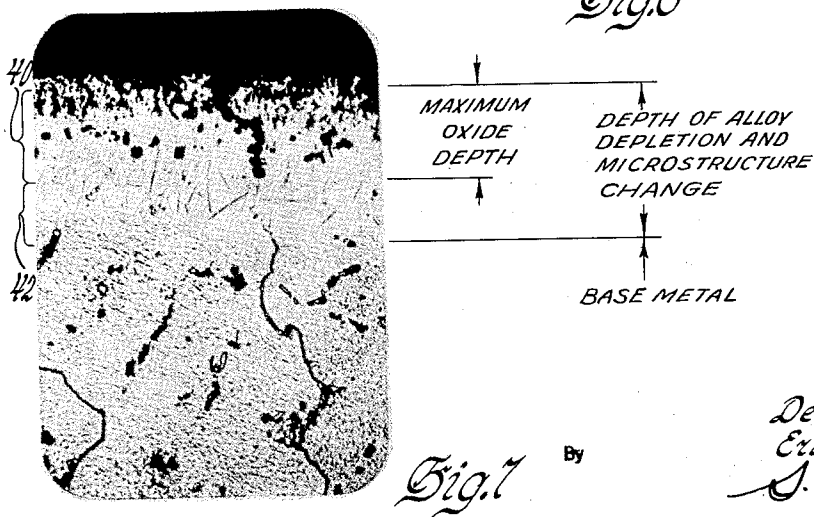
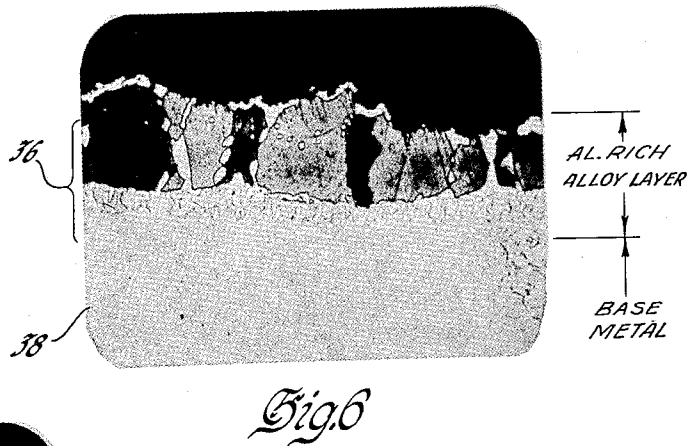
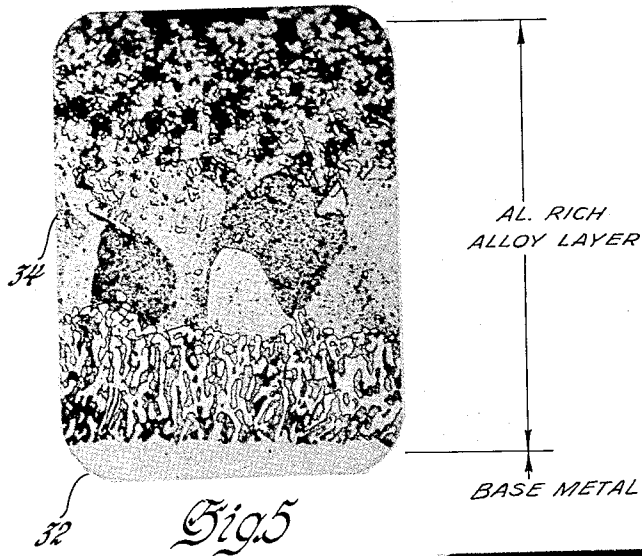
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OXIDATION-RESISTANT TURBINE BLADES

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3 Sheets-Sheet 2



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OXIDATION-RESISTANT TURBINE BLADES

Filed Oct. 11, 1956

3 Sheets-Sheet 3

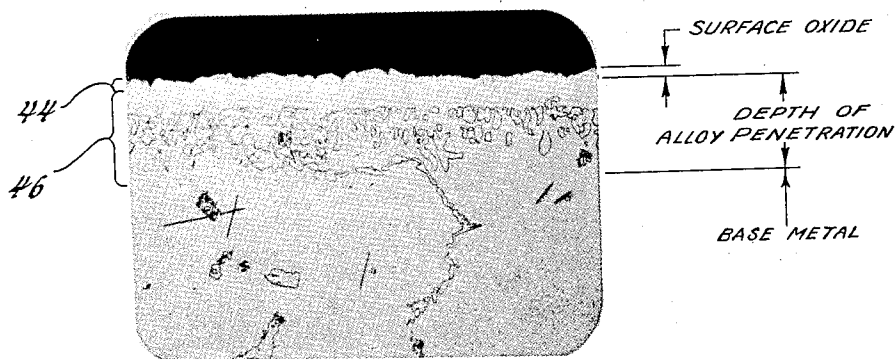


Fig. 8

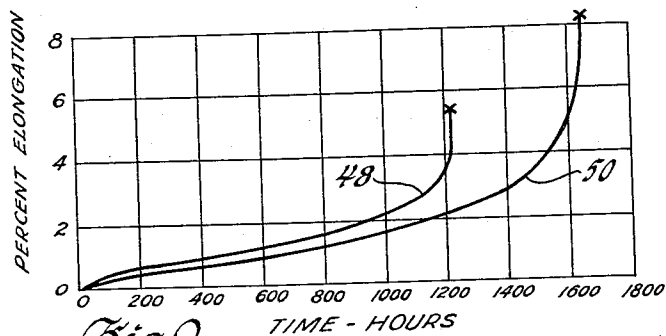


Fig. 9

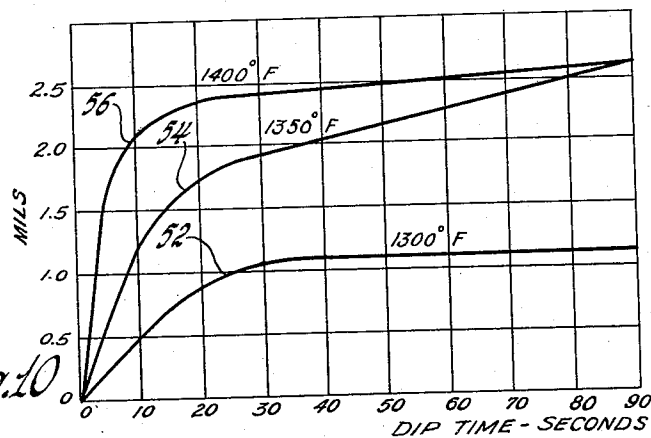


Fig. 10

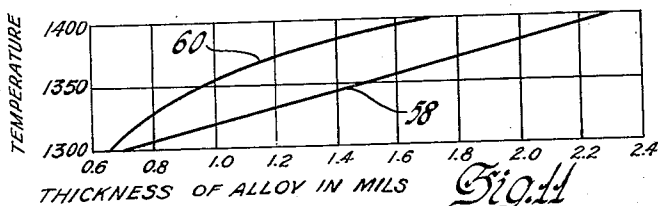


Fig. 11

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3,000,755

OXIDATION-RESISTANT TURBINE BLADES

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Filed Oct. 11, 1956, Ser. No. 615,417
15 Claims. (Cl. 117—51)

This invention relates to oxidation-resistant turbine buckets and nozzle guide vanes for gas turbine engines. More particularly, the invention is concerned with nickel base alloy and cobalt base alloy turbine buckets having surfaces provided with a protective layer of an alloy of the base metal with aluminum. The present application is a continuation-in-part of our co-pending patent application Serial No. 506,201, which was filed on May 5, 1955, now abandoned.

High-temperature alloy components, such as turbine buckets and nozzle guide vanes, of gas turbine engines are subjected to extended periods of service at elevated temperatures under variable stress conditions. When such components are formed of certain high-temperature nickel base alloys and cobalt base alloys, they possess excellent strength under most high-temperature service conditions. However, durability of these turbine buckets and nozzle guide vanes is materially reduced because of inadequate resistance to oxide penetration. As a result, maximum use cannot be made of such high strength alloys, despite their outstanding capacity to sustain high stresses at elevated temperatures under non-oxidizing conditions.

Moreover, as the operating temperatures of gas turbines of the type used in turbo-jet and turbo-prop engines are increased, the problem of oxidation of gas turbine buckets becomes more acute. Today, turbine engine manufacturers are designing gas turbine engines having operating temperatures as high as approximately 1900° F. At this very high temperature, oxidation of the nickel base and cobalt base alloys of which turbine buckets and nozzle guide vanes are conventionally formed seriously restricts the operating life of gas turbine engines. Nevertheless, such high-operating temperatures are desirable in order to obtain maximum thrust from the engines.

A principal object of the present invention, therefore, is to provide a turbine blade which will withstand higher operating temperatures than those presently being used. A further object of the invention is to eliminate oxidation of the base metal constituents, particularly along grain boundaries or preferred crystallographic planes, of nickel base alloy and cobalt base alloy gas turbine buckets and nozzle guide vanes. A still further object of the subject invention is to provide such turbine engine components with this protection without adversely affecting the load-carrying ability of the base alloy.

Another object of the invention is to provide nickel base alloy and cobalt base alloy turbine blades with a protective surface layer which possesses sufficient ductility to yield with the base metal when the latter is expanding, contracting, or stretching due to creep elongation under stress at elevated temperature. A further object of this invention is to provide a turbine bucket formed of nickel base alloy or cobalt base alloy and having, at its exposed surfaces, an integral layer of aluminum with the base material which affords effective protection against high-temperature oxidation. Although, in the case of a nickel base alloy, this layer is referred to herein as an "aluminum-nickel" layer or an "aluminum-nickel alloy" layer, it will be understood that the layer consists essentially of aluminum in combination with all the various constituents in the nickel base alloy of which the blade is formed. Analogous terminology is similarly employed to describe the protective surface layer formed

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on cobalt base alloys. Examples of suitable nickel base alloys and cobalt base alloys are hereinafter set forth.

A still further object of the present invention is to provide a process for forming a thin stable layer of the aforementioned type of aluminum-nickel alloy or aluminum-cobalt alloy at the surfaces of turbine buckets and nozzle diaphragms formed of nickel base alloys or cobalt base alloys, as the case may be, in such a manner that this layer will not flake or spall during the normal operating life of the engine in which these blades are installed.

The above and other objects are attained in accordance with this invention by providing a thin aluminum coating on surfaces of nickel base alloy and cobalt base alloy turbine buckets and nozzle guide vanes. On diffusion heat treatment, this aluminum coating further combines with the base alloy to form a layer of aluminum-nickel alloy or aluminum-cobalt alloy. Of course, some of the aluminum usually remains on the surface of this layer in the form of a thin overlay of aluminum oxides. The diffused aluminum-nickel alloy and aluminum-cobalt alloy layers are tough, resilient and possess good ductility. Under operating conditions, these alloy layers prevent oxide penetration of the base material, thereby improving the durability of the turbine buckets under high-temperature operating conditions. This protection is provided under static stress conditions, non-load conditions, impact load conditions, or hot working or forging conditions.

While the invention is hereinafter specifically described principally in connection with nickel base alloy turbine blades, it will be understood that the process set forth is also applicable to cobalt base parts.

Other objects and advantages of the present invention will more fully appear from the following detailed description of preferred embodiments of the invention, reference being made to the accompanying drawings, in which:

FIGURE 1 is an elevational view, with parts broken away and in section, of a turbine bucket formed of a nickel base alloy provided with an aluminum-nickel surface layer in accordance with the invention;

FIGURE 2 is a photomicrographic view of a high-temperature creep-resistant nickel base alloy, showing the metallographic structure of the alloy near its working surface after it had been exposed to cyclic heating at elevated temperatures;

FIGURE 3 is a photomicrographic view of the nickel base alloy shown in FIGURE 2 provided with a surface layer of aluminum-nickel alloy in accordance with this invention;

FIGURE 4 is a photomicrographic view of the alloy shown in FIGURE 3 having an outer aluminum-nickel layer in accordance with the invention, showing its metallographic structure after exposure to cyclic heating at elevated temperature;

FIGURE 5 is a photomicrographic view of the coated alloy shown in FIGURE 3 which had been heat treated prior to testing, showing its metallographic structure after exposure to cyclic heating at elevated temperature;

FIGURE 6 is a photomicrographic view of the coated alloy shown in FIGURE 3 which had been treated by a pickling process prior to heat treatment and testing, showing its metallographic structure after exposure to cyclic heat at elevated temperature;

FIGURE 7 is a photomicrographic view of the uncoated nickel base alloy shown in FIGURE 2 after being subjected to a stress-rupture test at elevated temperature;

FIGURE 8 is a photomicrographic view of the coated nickel base alloy shown in FIGURE 5 after being subjected to a similar high-temperature stress-rupture test;

FIGURE 9 is a graph comparing time-elongation characteristics at elevated temperature of an uncoated nickel

base alloy stress-rupture bar with a stress-rupture bar of the same alloy provided with a surface layer of aluminum-nickel alloy in accordance with the invention;

FIGURE 10 is a graph showing the effect of dipping temperature and time on the thickness of the diffused aluminum-nickel alloy layer; and

FIGURE 11 is a graph showing, after heat treatment, the effect of aluminum coating bath temperature and composition on the thickness of the diffused aluminum-nickel alloy layer.

The layer of aluminum-nickel alloy or aluminum-cobalt alloy, as the case may be, may be provided at the surfaces of the nickel base or cobalt base turbine bucket or nozzle diaphragm in any desired manner. The preferred method is to apply molten aluminum or aluminum base alloy to the turbine blade under conditions such that the aluminum will form an alloy with the nickel or cobalt and result in the desired alloy layer thickness. Best results are obtained when the aluminum or aluminum base alloy is applied by any of the procedures described in United States Patent No. 2,569,097, Grange et al., owned by the assignee of the present invention.

An especially advantageous method comprises preheating the turbine blade to a temperature between approximately 1280° F. and 1400° F. in a fused salt bath consisting essentially of 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na_2AlF_6 and 0.5% to 12% AlF_3 . The heated turbine blade is thereafter immersed for a short time in a molten bath of aluminum or aluminum base alloy at a temperature of about 1250° F. to 1325° F. Ordinarily, the turbine blade being coated is retained in the molten aluminum or aluminum base alloy not more than approximately 10 seconds, a period between 5 and 10 seconds being preferred at present.

Subsequently, the turbine blade is removed from the aluminum bath and rinsed for a short period of time not in excess of approximately 15 seconds in the fluxing salt. Best results are obtained if the total dip time in the aluminum coating bath and the subsequent salt bath is between 10 and 20 seconds. The excess coating material, which is still in a semi-molten or mushy condition, is then removed by rapidly vibrating the turbine blade, preferably while it is still immersed in the salt. Alternatively, an air blast may be employed to remove the surplus coating material. As thus treated, the turbine blade is provided with an extremely thin and uniform coating of aluminum bonded to the nickel base metal or cobalt base metal by an intermediate extremely thin and uniform layer of an alloy of aluminum-nickel or aluminum-cobalt.

The surfaces of the turbine blade to be coated are preferably cleaned prior to the aluminum coating and alloying operation. One satisfactory method is to clean the blade in a molten electrolytic caustic salt (such as the commercially available product called Kolene) at a temperature of about 900° F. The blade then may be washed in water and thereafter preferably further cleaned by acid pickling. A suitable acid pickling bath is an aqueous solution containing about 2% hydrofluoric acid, 7% sulfuric acid and 10% nitric acid. In some instances, the turbine blade may require only a simple degreasing treatment in a chlorinated solvent prior to the aluminum coating and alloying operation. Mechanical cleaning methods, such as grit blasting, sand blasting, hydroblasting, etc., may be employed in some cases to supplement the chemical treatment.

The steps of degreasing and pickling the turbine blade are not essential to the process, however, as heating in the fused salt prior to immersion in the aluminum or aluminum base alloy bath will provide the turbine blade with clean surfaces unless it had been exceptionally contaminated initially.

After the nickel base or cobalt base turbine blade has been cleaned, any portions thereof which are not to be coated, such as the attaching portions at the base of the blade, may be treated with a suitable stop-off coating

to prevent the aluminum from bonding to or alloying with the base metal at such surfaces. A suitable stop-off material for this purpose is a sodium silicate solution, such as an aqueous solution containing 20% to 50% sodium silicate.

It will be understood that variations in the aluminum coating method hereinbefore described may be made without departing from the scope of the present invention. For example, the aluminum may be applied to the turbine blade in the form of a paste or paint as described in co-pending patent application S.N. 459,093, Thomson et al., filed on September 29, 1954, now Patent No. 2,885,304. An example of the aluminum paste or paint which may be used is a mixture of aluminum powder with suitable amounts of a vehicle, such as low ash content lacquer or resin solution, liquid Lucite or a water solution of salt flux. Thus, aluminum powder may be mixed with a suitable resinous carrier, such as vinyl or acrylic resins in appropriate organic solvents, and applied by brushing, spraying or other appropriate means. A wetting agent also may be included in the slurry. The viscosity of the paste or paint used is determined by the amount and type of the solvent employed. If a flux is mixed with the aluminum powder, it is advantageous to employ a salt flux which is capable of fluxing or cleaning the nickel base or cobalt base alloy. Hence, an aqueous solution of the salt hereinbefore described as constituting the fluxing or heating bath may be advantageously employed as a vehicle for the aluminum powder. Moreover, a combination of resins or lacquers, salt fluxes and organic liquid vehicles may be mixed with aluminum powder to form the desired paste.

Vinyl resins and acrylic resins are among the lacquers or resins which may be used in the aluminum paste or spray. The lacquer identified as Binder Solution B-9571, currently manufactured and sold by Pierce & Stevens, Inc., is an example of an appropriate resinous binder. This type of binder normally contains about 4% or 5% solids and 95% solvent. The percentage of the solid resinous constituents is not as important as the volatility of the solvent, however, since high volatility is required to permit rapid drying of the paste after it has been applied to the turbine blade. Good results are obtained when approximately 30% to 50% by volume of aluminum powder, preferably between 200 and 400 mesh, is mixed with 10% to 20% by volume of binder solution and about 30% to 50% by volume of an appropriate thinner or solvent. Acetone or other conventional commercial thinners may be employed. It will be appreciated, of course, that the above ranges of the constituents in the paste composition are not critical and that a very wide variation in the composition may be used to obtain satisfactory results.

Alternatively, the aluminum may be hot sprayed onto surfaces of the nickel base or cobalt base turbine blade, this method commonly being referred to as metallizing.

Whether the aluminum is applied in the form of a paste or paint or as a hot spray, proper bonding of the aluminum coating material to the nickel base alloy or cobalt base alloy may be effected by subsequent heating, such as by immersion in the aforementioned salt bath. The paste should be allowed to dry before immersing the turbine blade in the salt so as to avoid introducing volatile matter into the hot salt. This bath provides proper fluxing of the nickel base alloy or cobalt base alloy and simultaneously melts the coating metal or keeps it in a molten state so as to distribute the aluminum thinly and evenly over the turbine blade. The molten salt thus prevents the formation of detrimental oxides which might otherwise adversely affect the resultant bond at the interface of the aluminum-nickel alloy or aluminum-cobalt alloy and the base metal.

The aluminum or aluminum base alloy coating material should contain approximately 80% or more aluminum in order to provide nickel base and cobalt base turbine blades with effective high-temperature oxidation resist-

ance. Hence, the word "aluminum," when used in the claims to refer to the coating material, is intended to include not only pure aluminum and commercially pure aluminum, but also aluminum base alloys containing at least approximately 80% aluminum. As hereinafter explained, an alloy consisting essentially of approximately 2% iron and the balance aluminum provides excellent results.

Turbine rotor buckets, nozzle guide vanes and stator blades are all forms of turbine blades which are exposed to high operating temperatures in gas turbine engines, particularly of the axial flow type. All of these parts may be formed of high-temperature creep-resistant nickel base alloys and cobalt base alloys provided with an aluminum-nickel or aluminum-cobalt surface layer in accordance with the present invention. Accordingly, the term "turbine blades" is employed herein as encompassing these various types of gas turbine engine components.

The aluminum-nickel alloy protective layer should in every instance be extremely thin. In general, the layer of this alloy should have a thickness of from approximately 0.0005 inch to 0.0025 inch. An aluminum-nickel layer 0.0012 inch to 0.0020 inch thick is preferred, however, with a layer thickness of about 0.0015 inch being considered optimum. Similar thicknesses are appropriate in the case of the aluminum-cobalt alloy protective layer. The thickness of the outer aluminum layer initially formed should not be in excess of approximately 0.004 inch, and it is presently preferred that this layer have a thickness less than about 0.0015 inch.

The following Table I contains examples of suitable high-temperature, creep-resistant nickel base alloys which may be satisfactorily provided with a thin, protective surface layer of aluminum-nickel in accordance with the present invention, the compositions being listed in percent by weight:

Table I

	Example 1	Example 2	Example 3	Example 4	Example 5
Carbon.....	¹ 0.15	0.35-0.45	¹ 0.07	0.15	¹ 0.08
Manganese.....	¹ 1	2-3	¹ 1	¹ 1	0.8-1
Chromium.....	15.5-17.5	23.5-26.5	19.5	19	14-16
Cobalt.....	¹ 2.5	10-15	13.5	10	-----
Molybdenum.....	16-18	2-4	4.25	10	-----
Tungsten.....	3.75-5.25	6-8	-----	-----	-----
Iron.....	4.5-7	15	12	15	5-9
Vanadium.....	0.2-0.6	-----	-----	-----	-----
Titanium.....	-----	-----	2.5	2.5	2.25-2.75
Aluminum.....	-----	-----	1.25	0.87	0.4-1
Silicon.....	¹ 1	¹ 1	1 0.75	1 0.65	¹ 0.5
Sulfur.....	-----	1 0.03	-----	-----	¹ 0.01
Copper.....	-----	-----	-----	-----	¹ 0.2
Nickel.....	Balance	Balance	Balance	Balance	Balance

¹ Max.

However, the nickel base alloy disclosed in United States Patent No. 2,688,536, Webber et al., appears to be the most outstanding turbine bucket material currently available with respect to stress-rupture properties, creep resistance, ductility and high-temperature corrosion resistance when provided with a surface layer of aluminum-nickel in accordance with this invention. This alloy comprises approximately 0.06% to 0.25% carbon, 13% to 17% chromium, 4% to 6% molybdenum, 8% to 12% iron, 1.5% to 3% titanium, 1% to 4% aluminum, 0.01% to 0.5% boron and the balance substantially all nickel. For some applications the aluminum content may be increased to approximately 6% and the iron content may be as low as 0.1% or as high as 35%. The alloy usually should not contain more than 20% iron, however. Normally manganese and silicon not in excess of 1% each are also included in the alloy.

Examples of high-temperature cobalt base alloys which may be provided with a thin, protective surface layer of aluminum-cobalt by the process herein are listed in the following Table II, the composition again being given in percentages by weight:

Table II

	Example 1	Example 2	Example 3	Example 4
5 Carbon.....	0.20-0.35	0.45-0.60	¹ 0.20	0.32-0.42
Manganese.....	-----	-----	1.00-2.00	0.60-1.80
Silicon.....	-----	-----	¹ 0.60	0.30-0.90
Sulfur.....	-----	-----	¹ 0.04	-----
Chromium.....	25.00-30.00	23.00-28.00	20.00-22.00	19.00-21.00
Nickel.....	1.50-3.50	9.00-12.00	18.00-22.00	19.00-21.00
10 Molybdenum.....	4.50-6.50	-----	2.50-3.25	3.50-4.50
Tungsten.....	-----	6.00-9.00	2.00-3.00	3.50-5.00
Columbium.....	-----	-----	0.75-1.25	3.00-4.50
Nitrogen.....	-----	-----	0.08-0.16	-----
Iron.....	¹ 2.00	¹ 2.00	-----	¹ 5.00
Cobalt.....	Balance	Balance	18.00-22.00	40.00-44.00

¹ Max.

Referring more particularly to the drawings, in FIGURE 1 is shown a turbine bucket 10 for a gas turbine of the axial flow type. In accordance with the invention this turbine bucket is formed of a nickel base alloy 12 provided with a surface layer 14 of aluminum-nickel alloy. For purposes of description the thickness of this alloy layer is considerably exaggerated in FIGURE 1, the actual thickness being in the order of only one- or two-thousandths of an inch, as hereinbefore explained.

It usually is unnecessary to provide the aluminum-nickel layer over the fastening portion 16 of the turbine bucket.

In order to fully understand the beneficial results provided by the surface layer of aluminum-nickel, the metallographic structure of nickel base alloys having this layer should be compared with similar alloys which do not have this layer. Thus, reference is made to the photomicrograph of FIGURE 2, showing the surface of a tip of a wedge specimen formed of an uncoated nickel base alloy 18 having the preferred composition set forth above which has been exposed to 197 hours of cyclic heating to 1800° F. This heating has resulted in oxide penetration to the approximate depth indicated by the reference numeral 20 in FIGURE 2. The oxide affected zone does not have the same desirable high-temperature properties that the nickel base alloy initially possessed. Moreover, associated with the oxide penetration is a zone 22 of a needle-like microconstituent beneath the oxide layer.

This zone, which is located at a progressively greater depth as the depth of oxide penetration is increased, is extremely brittle and possesses low stress-rupture properties. The formation of this microconstituent is accompanied by disappearance of the normal intermetallic network found in all as-cast components and is believed to be formed by a combination of degeneration of the intermetallic network and precipitation from the matrix. Dissolved oxygen and nitrogen gases are believed to be a factor in the formation of the needle-like microconstituent.

The microstructure of a similar nickel base alloy 24 having a surface layer of aluminum-nickel alloy 26 in accordance with the invention is shown in FIGURE 3. When a tip of a wedge specimen having such a layer is subjected to the type of cyclic heating hereinbefore described, the oxide penetration in the base metal is completely eliminated. Instead, as can be seen in FIGURE 4, the surface of a nickel base alloy 28, which has been aluminum coated in the above-described manner, has a relatively deep aluminum-rich alloy layer 30 which protects the base metal from the oxidizing gases. The specimen shown was exposed to 200 hours cyclic heating to 1800° F. Thus, nickel base alloys having the surface layer of aluminum-nickel not only are completely protected against the aforementioned oxide penetration but, after exposure to cyclic heating, also shown no evidence of the needle-like micro-constituent associated with oxide penetration. This desirable result may be attributed to the formation of a protective oxide film upon the surface of the nickel base alloy and resistance to the diffusion of gases into the matrix by the diffused aluminum atoms in solid solution with the nickel base metal.

This surface oxide layer appears to the naked eye to be similar to the surface oxide layers on uncoated specimens which have been exposed to the same high temperature test conditions. However, micro-examination reveals that the surface oxide layer on the coated specimens does not penetrate through the alloy layer into the nickel base metal.

Diffusion heat treatment of the turbine blades after the aluminum coating operation may be beneficially employed to reduce the aluminum concentration in the surface alloy layer. Such a heat treatment is highly desirable to maintain high-temperature properties of the nickel base turbine blades, and it does not adversely affect the surface protection afforded by the aluminum coating. In general, a diffusion heat treatment at approximately 1700° F. to 2350° F. for one to six hours has proved to be effective, while a diffusion period of three to six hours at a temperature between 1800° F. and 2100° F. is preferred at present. Highly satisfactory results have been obtained by a five hour diffusion heat treatment at 1800° F., followed by air cooling. A one to three hour heat treatment at a temperature of 2000° F. to 2150° F. is also very effective. It is desirable to subsequently vapor blast the turbine blades for inspection purposes. The photomicrograph of FIGURE 5 shows a wedge specimen of a nickel base alloy 32 which had been subjected to the aforementioned type of diffusion heat treatment and thereafter exposed to 200 hours of cyclic heating to 1800° F. The resultant differences in the microstructure of this specimen, particularly the increased depth of the aluminum-rich alloy layer 34, as compared with the thickness of the layer 30 in FIGURE 4, is readily apparent.

Stress-rupture tests were conducted on both untreated nickel base alloy test specimens and similar specimens provided with a surface layer of aluminum-nickel in accordance with the present invention. Microexamination was conducted on specimens sectioned from test bars which were stress-rupture tested at 1700° F. and 10,000 pounds per square inch. The total time at 1700° F. included a twenty hour pre-heat period before application of the load. All test bars had been investment cast in the same mold, and results were obtained on both uncoated and aluminum coated bars for direct comparison of the coating upon high-temperature properties.

When a nickel base alloy specimen was successively dipped in molten aluminum and the salt flux for a total period of 30 seconds with no diffusion heat treatment being employed and subsequently tested at 1500° F., an aluminum-rich alloy layer having a thickness of 0.0045 inch to 0.005 inch was obtained. This alloy layer was the most brittle of the various types of aluminum-nickel layers formed on the specimens tested. This brittleness is due to the high aluminum concentration in the outer portion of the alloy layer produced at the low testing temperature of 1500° F. As a result of the alloying action of the aluminum coating, the diameter of the test specimen was increased approximately 0.002 inch to 0.006 inch. Stress-rupture properties were slightly decreased as a result of the aluminum coating which, of course, improved the high-temperature oxidation resistance of the nickel base specimen. The microstructure of this alloy after 200 hours of cyclic heating to 1800° F. is shown in FIGURE 4.

A test bar similar to that described in the aforementioned example was aluminum coated in the same manner and subsequently subjected to a five hour diffusion heat treatment at 1800° F. followed by air cooling. This procedure increased the thickness of the aluminum-rich alloy layer between 0.005 inch and 0.0056 inch. Moreover, this alloy layer, which is shown in FIGURE 5 after the specimen was exposed to 200 hours of cyclic heating to 1800° F., was more ductile than the layer shown in the photomicrograph of FIGURE 4. The surface of this heat treated specimen possessed less pronounced aluminum concentration at the surface than

the specimen shown in FIGURE 4 due to the higher diffusion temperature. However, the thick aluminum-rich alloy layer was subjected to some spalling. The diameter of the diffusion heat treated aluminum coated test bar was approximately 0.002 inch to 0.004 inch larger than the diameter of the bar prior to the application of aluminum. These combined steps of aluminum coating the nickel base alloy and subsequent diffusion heat treatment resulted in slightly decreasing the stress-rupture life of the test bar and slightly increasing its elongation under tensile stress.

When similar aluminum coated nickel base test specimens were subjected to a diffusion heat treatment of five hours at 2000° F. followed by air cooling, the aluminum-rich alloy layer increased in thickness to between 0.0056 inch and 0.0061 inch on the average. This layer was fairly ductile because of the low aluminum concentration at the surface due to the 2000° F. diffusion temperature. However, the thick layer was susceptible to some spalling. The increase in diameter of the test bars resulting from this aluminum coating and diffusion treatment averaged approximately 0.002 inch to 0.005 inch. These bars showed some decrease in stress-rupture life and an appreciable decrease in elongation under tensile stress.

Other nickel base specimens of the same composition were provided with a thin surface layer of aluminum-nickel alloy by means of a procedure which included successively pickling the aluminum coated specimens in acid and further diffusing the aluminum into the base metal by heat treatment. Test bars processed in this manner exhibited excellent stress-rupture properties. For example, it was found that the physical properties of nickel base alloy test bars were greatly improved when these bars were coated by means of a 10 second aluminum dip followed by a 10 second salt rinse and thereafter subjected to a treatment comprising a pickling period of 25 minutes in a 10% hydrochloric acid solution, five hours diffusion at 1800° F. and air cooling. A photomicrograph of a section of a test bar so treated is shown in FIGURE 6 after the specimen was exposed to 200 hours of cyclic heating to 1800° F. It will be noted that the aluminum-nickel layer 36 on the surface of the base metal 38 is relatively thin, the alloy layer being only about 0.0017 inch to 0.0019 inch thick. Of the various procedures which may be used to aluminum coat and heat treat nickel base alloys in accordance with the subject invention, this latter process produces the most ductile aluminum-rich alloy layer. Moreover, there is no indication that this layer tends to spall. Although a thinner layer of aluminum-rich alloy is thereby provided on the surface of nickel base alloys, this layer possesses a low aluminum concentration at the surface. This combination of a thin aluminum-rich layer and a low aluminum concentration at its surface provides the treated alloy with optimum physical properties with respect to stress-rupture characteristics and high-temperature oxidation resistance. Moreover, the above-described treatment does not measurably increase the diameter of a test bar.

Thus it will be seen that diffusion heat treatment after the aluminum coating step is highly desirable to maintain the high-temperature properties and to provide an alloy layer which is plastic at elevated temperature during deformation with no loss of oxidation resistance. This heat treatment produces these desirable results by reducing the aluminum concentration at the surface alloy layer.

As explained above, on the other hand, aluminum coated nickel base turbine blades which have not been subjected to diffusion heat treatment are provided with an aluminum-rich alloy layer over which there is an excess unalloyed aluminum layer. The thickness of the as-dipped aluminum-rich alloy layer may be controlled by varying the length of the total dip period. The term

"total dip period" is used herein as meaning the total exposure time of the immersed article to molten aluminum and includes the periods of immersion in both the aluminum coating bath and the salt flux. However, examination has indicated that the as-dipped aluminum-rich alloy layer does not solely control the final diffused layer thickness. The excess aluminum overlay, which forms more aluminum-rich alloy in the diffusion process, has a greater influence on the final layer thickness. Although vibration of the turbine blades in the salt bath removes some of the excess aluminum, an appreciable amount of the excess aluminum still remains on the surface of the blades.

Accordingly, to obtain optimum results by means of a thinner diffused layer of aluminum-nickel, it is advantageous to remove the excess aluminum overlay before diffusion. As indicated above, this can be effectively accomplished by pickling the as-dipped nickel base turbine blades in a dilute aqueous solution of hydrochloric acid at a temperature of about 60° F. to 90° F. for approximately 15 minutes to 45 minutes. A 10% acid solution has been found to produce excellent results. The aluminum-rich alloy layer is not materially affected by this pickling process. Subsequent diffusion produces an alloy layer less than 0.002 inch thick, as compared with a layer thickness of approximately 0.005 inch to 0.006 inch for aluminum coating nickel base specimens which are not pickled before diffusion. Hence it can be seen that when the excess aluminum overlay is removed, the thickness of the final diffused aluminum-nickel layer is controlled by the thickness of the aluminum-rich alloy which is formed during dipping. Since this thickness may be controlled by varying the total time the nickel base alloy is immersed in the aluminum and the salt bath, we have found a total dip period of 10 to 20 seconds to be highly satisfactory. In this manner an aluminum coated nickel base turbine blade may be produced which possesses excellent stress-rupture and other physical properties, as well as corrosion resistance at elevated temperatures.

The photomicrograph of FIGURE 7 shows the microstructure of a stress-rupture bar formed of a nickel base alloy having the preferred composition hereinbefore set forth after the bar has been tested for 2807 hours at a temperature of 1700° F. under a stress of 8500 pounds per square inch. It will be seen that both the maximum oxide depth 40 and the depth of alloy depletion and microstructure change are appreciable. The latter zone is indicated in FIGURE 7 by the total depth of zone 40 and zone 42. When this stress-rupture bar is compared with the stress-rupture bar, such as the one shown in the photomicrograph of FIGURE 8, having the same base metal composition but provided with a diffused surface layer of aluminum-nickel in accordance with the invention, the differences in the microstructure of the two materials are readily apparent. This stress-rupture bar likewise was tested at 1700° F. under a stress of 8500 pounds per square inch, but the test was extended for 2919 hours. At the end of this test period, as shown in FIGURE 8, the thickness of surface oxide zone 44 is negligible. The depth of the aluminum-nickel alloy layer is indicated at 46.

Results of the above and other extended stress-rupture tests at temperatures between 1500° F. and 1700° F. indicate that the stress-rupture life of nickel base alloys is increased approximately 40% by the provision of a thin surface layer of aluminum-nickel by means of the preferred procedure described above. The aluminum-nickel layer eliminates oxide penetration of the base metal, and the diffusion treatment produces beneficial aging or precipitation in its microstructure. It is under these long-period high-temperature conditions that oxidation plays a major part in determining the life of a nickel base turbine bucket alloy.

The nickel base alloys shown in the photomicrographs of FIGURES 2 through 8 have the same composition,

i.e., the preferred composition hereinbefore described. The photomicrograph of FIGURE 7 is at 250 magnifications while the other photomicrographs are at 500 magnifications. Marble's reagent was used as the etchant for the specimens shown in FIGURE 2, Vilellos etch was employed in the specimens of FIGURE 6, while a modified acid ferric chloride was used as the etchant for the specimens shown in the other photomicrographs.

The graph of FIGURE 9 compares the creep elongation of the uncoated nickel base alloy, shown by the curve 48, with the creep elongation of the same alloy provided with the above-described surface layer of aluminum-nickel. The curve 50 indicates the creep characteristics of the latter material. A tensile load of 2500 pounds per square inch and a temperature of 1500° F. were employed in these tests. The increased life of the treated bars is reflected in a decreased creep rate, indicating that the strength of the alloy can be more effectively utilized by the formation of the protective layer. This is important when ductility is measured in terms of extremely long periods of time at elevated temperature. For example, an uncoated nickel base alloy specimen, when tested at a temperature of 1700° F. under a tensile load of 8500 pounds per square inch, deformed approximately 1.1% in 2807 hours, while a similar specimen provided with the aforementioned surface layer of aluminum-nickel showed no measurable deformation in 2919 hours.

It also has been found that the thickness of the final aluminum-nickel layer formed during diffusion treatment may be controlled to some extent by both the temperature of the aluminum dip bath and the composition of the aluminum coating material. The graph of FIGURE 10 indicates the effect of temperature and the length of the total dip period on the thickness of this layer. For example, the final diffused alloy layer on samples dipped in pure aluminum for the preferred immersion period of 10 to 20 seconds increases approximately 0.00015 inch for each 10° F. rise in dipping temperature from 1300° F. to 1400° F. This is shown in FIGURE 10 wherein the curves 52, 54 and 56 indicate aluminum bath temperatures of 1300° F., 1350° F. and 1400° F., respectively.

As indicated by the graph of FIGURE 11, if the total dipping time and dipping temperature remain constant, the presence of a small amount of iron in the aluminum coating bath tends to reduce the thickness of the diffused aluminum-nickel layer. In this graph the curve 58 shows the approximate thickness of this layer when commercial 2S aluminum is used as the coating material, while the curve 60 indicates the thickness of the aluminum-nickel layer when the aluminum coating material contains approximately 2% iron. When the preferred total dip time of 10 to 20 seconds is employed with a coating metal bath at a temperature of approximately 1350° F., the thickness of the diffused alloy layer on nickel base turbine blades coated with an alloy of 2% iron and 98% aluminum, for example, will be approximately 0.0005 inch less than the thickness of the aluminum-nickel layer formed by coating with pure aluminum.

While this invention has been described by means of certain specific examples, it will be understood that the scope of the invention is not to be limited thereby except as defined in the following claims.

We claim:

1. A method of making a high temperature oxidation-resistant turbine blade which comprises applying a coating metal selected from the class consisting of aluminum and aluminum base alloys to surfaces of a turbine blade formed of a base metal selected from the class consisting of nickel base alloys and cobalt base alloys, heating said blade to diffuse a portion of said coating metal into said base metal, removing excess coating metal from said surfaces with an acid solution, and thereafter heating said blade for a period of time sufficient to diffuse the remaining coating metal into said surfaces to form with the base metal of said turbine blade an oxidation-resistant

surface layer of an alloy of said coating metal and said base metal having a thickness not in excess of approximately 0.0025 inch.

2. A method of providing an oxidation-resistant alloy layer at surfaces of an article formed of a metal selected from the class consisting of nickel base alloys and cobalt base alloys, said method comprising applying a coating metal containing at least 80% aluminum to said surfaces, thereafter immersing said article for a short period of time in a fused salt bath capable of absorbing aluminum oxides, said salt bath being at a temperature of approximately 1280° F. to 1400° F. while the article is immersed therein, treating the coated surfaces of said article with an acid solution to remove a portion of said coating metal, and subsequently heating said coated article at a temperature of about 1700° F. to 2350° F. to diffuse said coating metal into said surfaces.

3. A method of providing a thin oxidation-resistant layer of aluminum-nickel alloy at surfaces of a nickel base alloy, said method comprising immersing the nickel base alloy in a fused salt bath activated by aluminum in contact therewith, subsequently immersing said alloy in a molten bath of a coating metal selected from the class consisting of aluminum and aluminum base alloys, thereafter removing the coated nickel base alloy from said coating bath, rinsing said coated alloy in said salt bath, thereafter treating the coated surface of said alloy with a hydrochloric acid solution to remove a portion of said coating metal from said alloy, and subsequently heating said coated alloy at a temperature of about 1700° F. to 2350° F. to cause extensive diffusion of said remaining coating metal into said alloy.

4. A method of providing a turbine blade formed of a nickel base alloy with an oxidation-resistant surface layer of aluminum-nickel alloy, said method comprising applying a layer of aluminum to the blade, immersing said blade for a period of time not in excess of 15 seconds in a molten salt capable of dissolving aluminum oxides, said salt being at a temperature between approximately 1280° F. and 1400° F. while said blade is immersed therein, removing said blade from said salt and permitting the molten aluminum on said blade to solidify, treating the solidified coating on said blade with a pickling solution for a period of time sufficient to remove from said blade substantially all of said coating which has not diffused into said nickel base alloy, and thereafter heating said blade at a temperature of about 1700° F. to 2350° F. for one to six hours to diffuse said aluminum into said nickel base alloy and form an aluminum-nickel diffusion layer having a thickness of approximately 0.0005 inch to 0.0025 inch.

5. A method of forming a thin oxidation-resistant layer of aluminum-nickel alloy on surfaces of an article formed of a nickel base alloy, said method comprising immersing said article in a fused salt bath comprising, by weight, approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na_3AlF_6 and 0.5% to 12% AlF_3 , said fused salt being activated by aluminum in contact therewith, subsequently immersing said article in a molten bath of a coating metal containing at least 80% aluminum, removing the coated article from said coating metal bath, treating the solidified coating thus formed on said article with an acid pickling solution for a period of time sufficient to remove from said article substantially all of said coating which has not diffused into said nickel base alloy, and thereafter heating said article for a short period of time to diffuse the coating metal into said nickel base alloy.

6. A method as in claim 5 in which the fused salt bath is maintained at a temperature within the range of approximately 1280° F. to 1400° F. while the nickel base alloy article is immersed therein.

7. A method as in claim 5 in which the temperature of the surface of the nickel base alloy article is at least as

high as the melting point of the coating metal while said article is immersed therein.

8. A method of providing a nickel base turbine blade with a thin protective surface layer of aluminum-nickel alloy, said method comprising applying a coating metal containing at least 80% aluminum to surfaces of said blade, thereafter immersing said blade in a molten salt comprising by weight approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na_3AlF_6 and 0.5% to 12% AlF_3 , said molten salt being activated by aluminum in contact therewith, the portion of said blade to be coated having a temperature at least as high as the melting point of said coating metal while in said activated salt, removing the coated blade from said salt and permitting the molten coating metal on said blade to solidify, thereafter treating the coated surfaces of said blade with an acid solution to remove excess coating metal therefrom, and subsequently heating said blade at a temperature of at least 1700° F. for a period of time sufficient to diffuse the remaining coating metal into said blade.

9. A method of forming a high-temperature oxidation-resistant turbine blade having a thin layer of aluminum-nickel alloy at its surfaces, said method comprising casting into the shape of a turbine blade a nickel base alloy comprising 0.06% to 0.25% carbon, 13% to 17% chromium, 4% to 6% molybdenum, 1% to 6% aluminum, 1.5% to 3% titanium, iron not in excess of 20%, boron not in excess of 0.5% and the balance substantially all nickel, removing foreign matter from surfaces of said casting, thereafter coating said surfaces with a thin layer of aluminum, immersing said coated blade in a fused salt bath capable of absorbing aluminum oxides, said bath being maintained at a temperature of approximately 1280° F. to 1400° F., subsequently agitating said blade while in said bath to distribute the molten aluminum over said blade, removing said blade from said salt bath and permitting the molten aluminum to solidify on said blade, treating said coated blade with a hydrochloric acid solution to remove a portion of said solidified aluminum from said blade, and thereafter heating said blade at a temperature of about 1700° F. to 2350° F. for one to six hours to extensively diffuse the remaining aluminum coating into said nickel base alloy.

10. A method of forming a high-temperature oxidation-resistant turbine blade which comprises cleaning a turbine blade formed of a metal selected from the class consisting of nickel base alloys and cobalt base alloys, preheating and fluxing said turbine blade in a molten salt bath at a temperature of about 1280° F. to 1400° F., thereafter dipping said turbine blade in a molten aluminum bath for a period of time not in excess of approximately 15 seconds to coat surfaces of said turbine blade with aluminum, rinsing said coated blade in a molten salt bath to drain excess aluminum therefrom, removing said coated blade from said salt bath, permitting said aluminum to solidify to thereby form on said base metal a thin aluminum oxide overlay bonded to said base metal by a thin intermediate diffused layer of an alloy of aluminum and the base metal, thereafter immersing said blade in an acid solution to remove at least a portion of said overlay from said blade, and subsequently heating said blade for at least one hour at a temperature sufficient to diffuse the remaining coating metal into said blade.

11. A method of forming a high-temperature oxidation-resistant turbine blade which comprises cleaning surfaces of a nickel base alloy turbine blade, preheating and fluxing said surfaces in a molten salt bath at a temperature of about 1280° F. to 1400° F., thereafter dipping said turbine blade in a molten aluminum bath at a temperature of approximately 1250° F. to 1325° F. for a period of time not in excess of approximately 15 seconds to coat said surfaces with aluminum, rinsing said blade in a molten salt bath for not more than 15 seconds to drain excess aluminum therefrom and to partially diffuse

said aluminum into said nickel base alloy, removing said blade from said salt bath and permitting said aluminum to solidify to thereby form on said nickel base alloy a thin aluminum oxide overlay bonded to said alloy by a thin intermediate diffused layer of aluminum-nickel alloy, thereafter immersing said blade in a hydrochloric acid solution to remove at least a portion of said overlay from said blade, and subsequently heating said turbine blade at a temperature of 1700° F. to 2350° F. for one to six hours to further diffuse said aluminum-nickel alloy layer.

12. A method of forming a high-temperature oxidation-resistant turbine blade which comprises preheating and fluxing surfaces of a cobalt base alloy turbine blade in a molten salt bath capable of absorbing aluminum oxides, said salt bath being at a temperature of 1280° F. to 1400° F., thereafter immersing said fluxed turbine blade in a molten aluminum bath at a temperature of 1250° F. to 1325° F. for a short period of time to coat said fluxed surfaces with aluminum, removing said coated blade from said aluminum bath, permitting the aluminum on said surfaces to solidify to thereby form on said cobalt base alloy a thin aluminum oxide overlay bonded to said alloy with a thin intermediate layer of aluminum-cobalt alloy, thereafter treating the coated surfaces of said blade with an acid solution to remove at least a portion of said overlay from said blade, and subsequently heating said blade at a temperature of 1700° F. to 2350° F. to further diffuse said aluminum-cobalt alloy layer into the base metal of said blade.

13. A method of forming a thin oxidation-resistant layer of aluminum-nickel alloy on surfaces of a turbine blade formed of a nickel base alloy, said method comprising immersing the nickel base alloy turbine blade for a short period of time in a fused salt bath comprising, by weight, approximately 37% to 57% KCl, 25% to 45% NaCl, 8% to 20% Na₃AlF₆ and 0.5% to 12% AlF₃, said fused salt being at a temperature within the range of approximately 1280° F. to 1400° F. and activated by aluminum in contact therewith, subsequently immersing the turbine blade for about 5 to 10 seconds in a molten bath of a coating metal of the class consisting of aluminum and aluminum base alloys, said coating metal bath being at a temperature between approximately 1250° F. and 1325° F., thereafter immersing said turbine blade in said fused salt bath for a period of time not in excess of 15 seconds, vibrating said coated turbine blade while in said salt bath to remove excess coating metal therefrom, the total immersion time of said turbine blade in said coating metal bath and said subsequent salt bath being between 10 and 20 seconds, removing said turbine blade from said salt bath and permitting the coating metal to solidify on said blade to form a thin diffusion zone of aluminum-nickel alloy at surfaces of said nickel base alloy, thereafter pickling said turbine blade for approxi-

mately 15 minutes to 45 minutes in a dilute aqueous solution of hydrochloric acid at a temperature of about 60° F. to 90° F. to remove excess solidified coating metal from surfaces of said blade, and finally further diffusing the aluminum in said layer by heating said blade in a gaseous atmosphere for three to six hours at a temperature between 1800° F. and 2100° F.

14. A method of treating a turbine blade formed of a base metal selected from the class consisting of nickel base alloys and cobalt base alloys to increase its oxidation resistance at elevated temperature, said method comprising applying a coating metal selected from the class consisting of aluminum and aluminum base alloys to surfaces of said turbine blade, heating said blade to diffuse a portion of said coating metal into said base metal, treating the solidified coating on said surfaces with an acid pickling solution for a period of time sufficient to remove from said surfaces substantially all of said coating which has not diffused into said base metal, and thereafter heating said treated blade for a period of time sufficient to further diffuse said coating metal into said surfaces to form with the base metal of said blade an oxidation-resistant surface layer of an alloy of said coating metal and said base metal.

15. A method of treating a turbine blade to increase its oxidation resistance at elevated temperature, said method comprising applying a coating metal selected from the class consisting of aluminum and aluminum base alloys to surfaces of a turbine blade formed of a base metal selected from the class consisting of nickel base alloys and cobalt base alloys, heating said blade to diffuse a portion of said coating metal into said base metal, pickling said coated blade with an acid solution to remove from said blade most of the solidified coating which has not diffused into said base metal, and thereafter heating said treated turbine blade at a temperature of at least 1700° F. for a period of time sufficient to further diffuse said coating metal into said surfaces to form with the base metal of said blade an oxidation-resistant surface layer of an alloy of said coating metal and said base metal.

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