

Jan. 19, 1971

S. G. BERKLEY ET AL

3,556,744

COMPOSITE METAL ARTICLE HAVING NICKLE ALLOY HAVING
COATS CONTAINING CHROMIUM AND ALUMINUM

Filed Aug. 16, 1965

2 Sheets-Sheet 1

FIG. 1

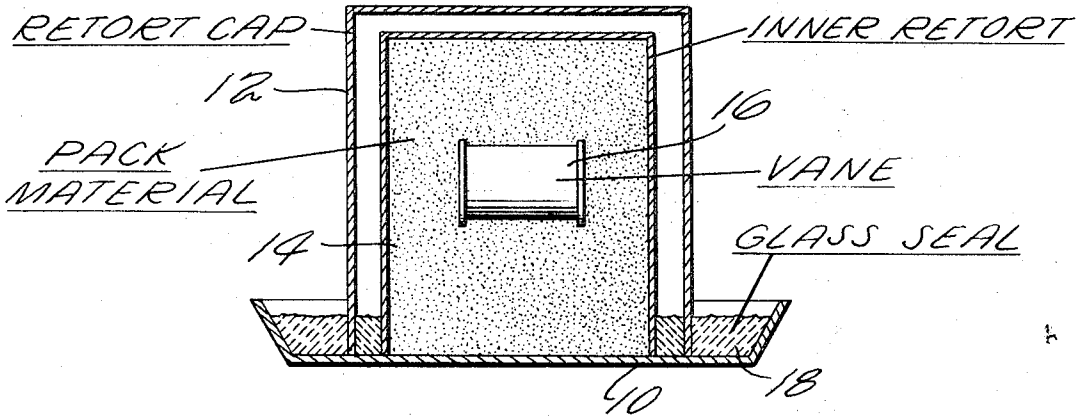


FIG. 2

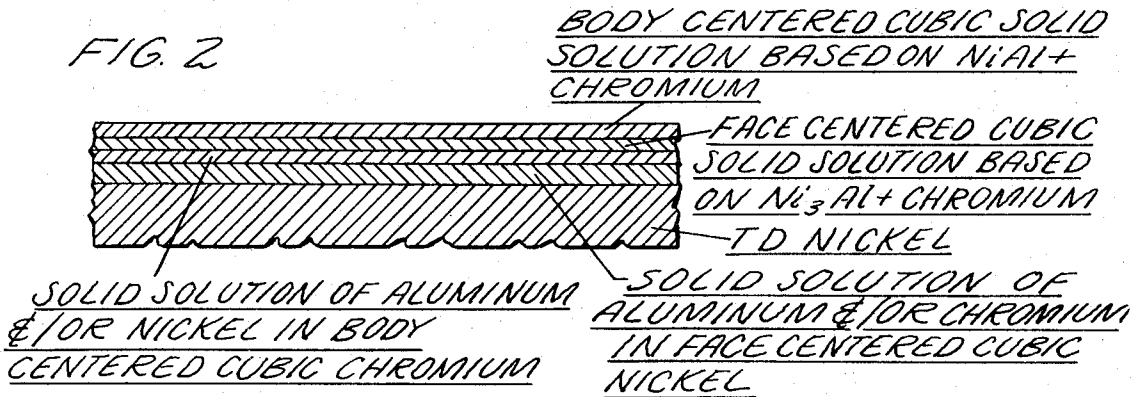
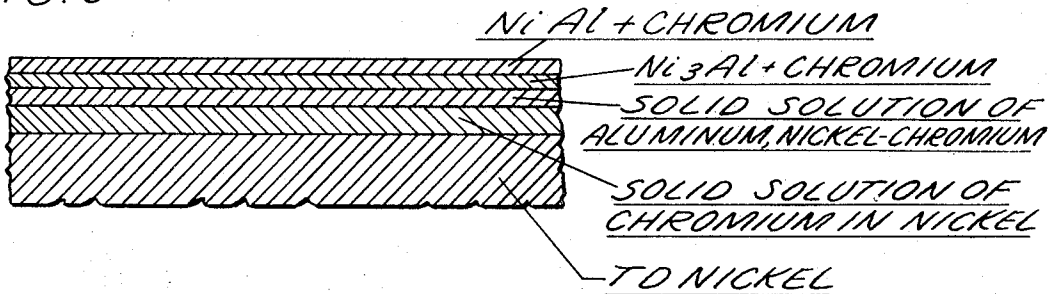


FIG. 3



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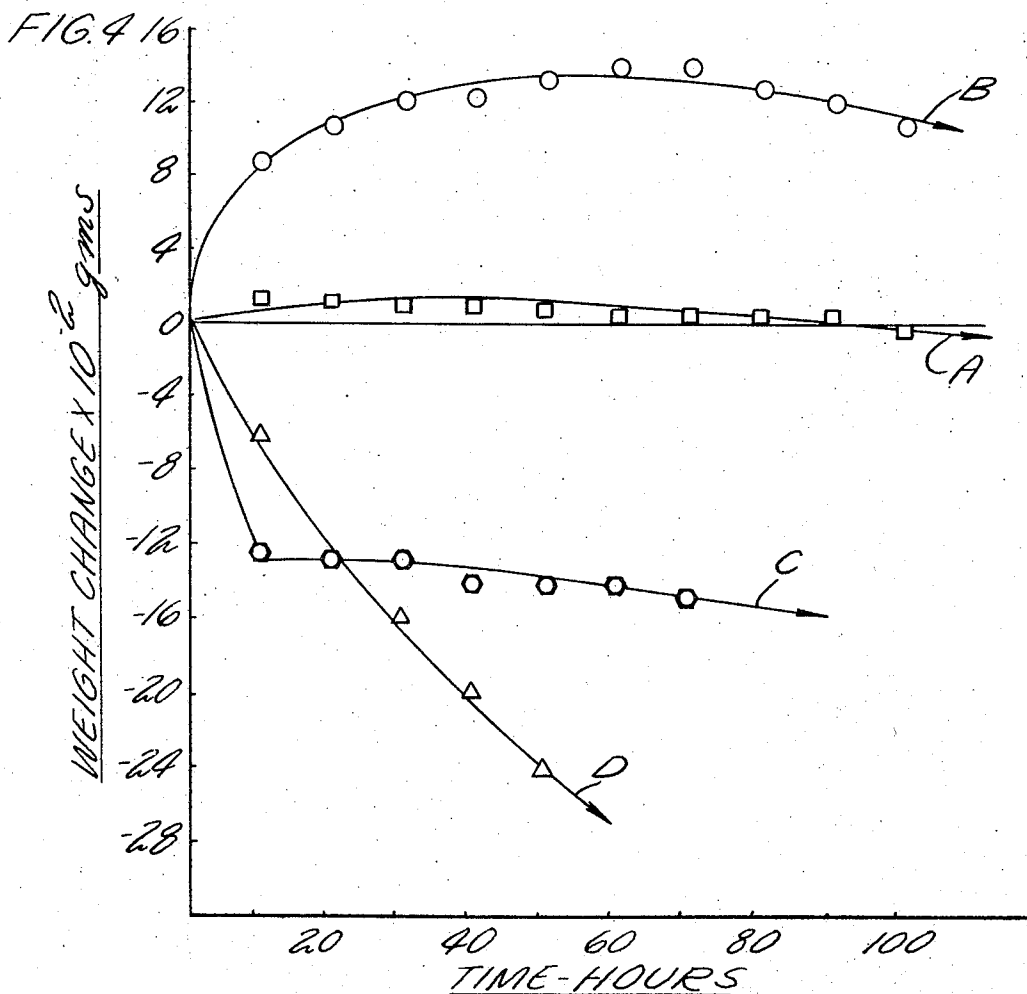
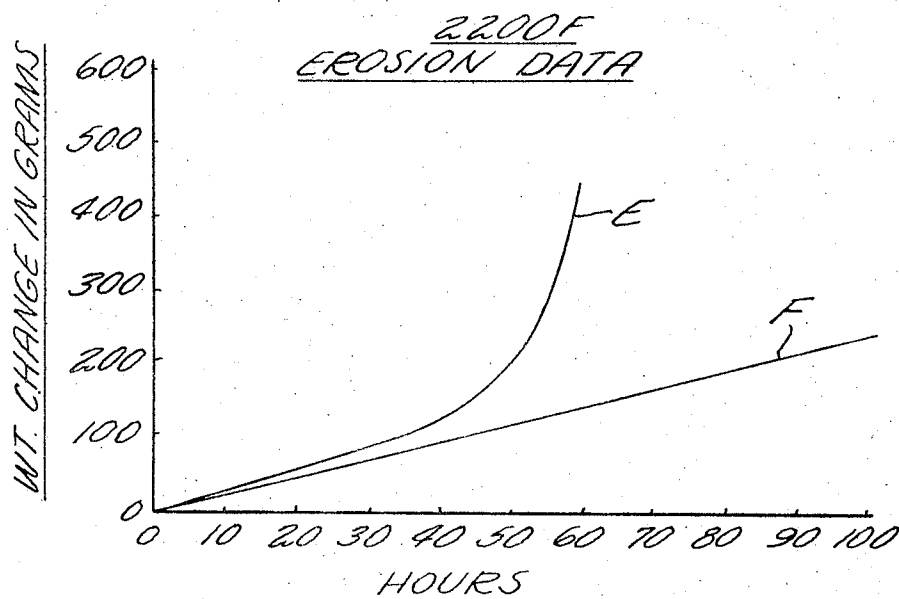


FIG. 5



1

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COMPOSITE METAL ARTICLE HAVING NICKEL ALLOY HAVING COATS CONTAINING CHROMIUM AND ALUMINUM

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Filed Aug. 16, 1965, Ser. No. 480,029

Int. Cl. B32b 15/00

U.S. Cl. 29—183.5

5 Claims

ABSTRACT OF THE DISCLOSURE

An article and a method for producing an article having high-temperature resistance. An alloy from the group consisting of nickel base, cobalt base and iron base alloys is provided with a chromium coating by a dispersion method and a second chromium-aluminum method by the same dispersion method.

The present invention relates to a novel and improved process for protecting metallic members of dispersion strengthened alloys against oxidation, corrosion and erosion in operation at relatively high temperatures, often above 2,200° F., and to the novel products of such process.

Objects and advantages of the invention will be set forth in part hereinafter and in part will be obvious herefrom, or may be learned by practice with the invention, the same being realized and attained by means of the steps, process and compositions pointed out in the appended claims.

The invention consists in the novel steps, process, compositions and improvements herein shown and described.

The present invention has for its object the provision of a novel and improved process for providing high-temperature resistant alloys with protective coatings which enable the coated members to withstand exposure to severe environmental conditions at elevated temperatures over relatively long periods of time. A further object of the invention is the provision of coated members formed from dispersion-strengthened alloys which show improved properties in actual use at elevated temperatures and under severe erosive and corrosive conditions.

Still another object is the provision of a novel and improved process for the production of gas-turbine blades and vanes and other turbine structures from some of the so-called "dispersion strengthened alloys," such as "TD Nickel," by providing such blades, vanes or structures with a corrosion and erosion-resistant coating so that the good mechanical properties of the TD Nickel or other alloy are retained, at the same time that the surface of the alloy is fully protected against the corrosive and erosive action to which the blades or vanes are subjected in actual use.

Parts, such as blade and vane members for use in gas turbines and to be operated at relatively high temperatures, have heretofore been coated with various protective layers which greatly improve the properties and life of such blades and vanes. However, such coatings of the prior art have proved to be porous or subject to spalling on a dispersion-strengthened metal like TD Nickel so that the coatings are not completely protective over long periods of time under severe operating conditions.

2

According to the present invention, gas-turbine blades and vanes or other parts to be subjected to combustion gases under severe operating conditions of temperature and other factors are formed from an alloy which is adapted to be used at relatively high temperatures, such as are encountered in the operation of modern jet engines and gas turbines and are protected against excessive corrosion and erosion by a multi-layer coating of refractory materials which adhere strongly to the part and protect it against the corrosive and erosive attack of the hot combustion gases which impinge on it.

Many of the dispersion strengthened alloys which have superior mechanical properties at elevated temperatures, such as 2,000° F. or higher, are readily susceptible to oxidation, corrosion and erosion under normal operating conditions, and therefore cannot be successfully used in their normal condition. Heretofore, it has been suggested that these alloys should be coated with more refractory materials, but the coatings of the prior art, while advantageous, have proved to be unsatisfactory over long periods of severe operation due to the porosity of the coating or its tendency to break away from the underlying surface of the alloy, a condition which is referred to as "spalling."

According to the present invention, a member formed from an alloy preferably selected from the class of dispersion-strengthened nickel-base, cobalt-base and iron-base alloys is first coated with a thin layer of chromium, and then with a thin layer of an aluminum-chromium alloy, the coatings being bonded to each other by diffusion and the underlying chromium coating being diffusion-bonded to the surface of the alloy member.

Among the alloys to which the process of the present invention is applicable, and from which the products of the present invention may be formed are alloys such as "TD Nickel" (a Du Pont alloy consisting of 98% nickel and 2% dispersed thoria), other nickel base alloys consisting essentially of nickel and 20% chromium and 2% thoria, nickel plus 15% molybdenum and 2% thoria, nickel plus 20% chromium, 15% molybdenum and 2% thoria; all of which are dispersion-strengthened alloys. In place of thoria, other dispersion strengtheners such as alumina or zirconia, titania, magnesia, hafnia and the rare earth metal oxides may be employed.

Also useful are dispersion-strengthened alloys consisting essentially of nickel, chromium and thoria, nickel, molybdenum and thoria, and nickel, chromium, molybdenum and thoria, of which the following are exemplary:

Nickel, percent.....	78	83	63
Chromium, percent.....	20	-----	20
Molybdenum, percent.....	-----	15	15
Thoria, percent.....	2	2	2

The total thickness of the dual coatings of the present invention are from 0.001" to 0.01", preferably from 0.001" to 0.005", and are preferably formed on the surface of the alloy by packing the cleaned alloy parts in a mass of finely divided material composed of the chromium metal to form the coating and a small amount of an activator, and a substantially inert filler. Thereafter, the alloy part and the mass of powder are subjected to a diffusion heat treatment, preferably in a hydrogen atmosphere, at a temperature of from 1,800° to 2,550° F. or below the melting point of the alloy (2,650° F.) for a period of time, such as 15 minutes to 72 hours, preferably about 2 hours at 2,400° F. Where the alloy is treated in vacuum the inert filler may be omitted from the pack.

In lieu of packing the blade or vane in a powder mixture, the blade or vane may usually be provided with a coating of chromium by dipping or spraying the blade or vane in an aqueous slurry of the desired chromium powders, so that the part acquires a coating of such solids, after which it is dried and then subjected to the same heat treatment in vacuum or in an inert atmosphere as if packed in a powder bed, usually with an inert filler.

Thereafter the alloy part is removed from the powder mixture, any loose particles are removed, and the alloy part is subjected to a second coating process in another powder pack composed of finely divided aluminum metal and finely divided chromium metal, and with an inert filler and an activator powder, and the part is again subjected to heat treatment in an inert atmosphere, preferably hydrogen, for a period of from 15 minutes to 72 hours, preferably about 2 hours, at a temperature of from 1,000° to 2,550° F., preferably about 2,100° F. Here also, if the treatment is in a vacuum, the inert filler may be omitted.

The chromium powder used is preferably finely divided pure chromium metal, 100 mesh or finer, and it has been found desirable to exclude impurities such as sulfur and carbon which tend to interfere with the formation of a continuous, adherent coating which is highly resistant to corrosion and erosion at elevated temperatures.

The aluminum powder is also preferably finely divided aluminum metal, 100 mesh or finer, and relatively pure and substantially free from sulfur and carbon.

The inert powder or filler is generally finely divided alumina, although other inactive powdered materials may be used such as zirconia, titania, ceria, magnesia, hafnia and the rare earth metal oxides.

The activator powder includes a source of halogen such as chromic chloride, bromide, iodide or fluoride, sodium and potassium chloride, potassium fluoride, ammonium chloride, iodide or bromide, in finely divided form, preferably 100 mesh or finer.

While a hydrogen atmosphere is preferred during the heating steps, the heat treatment may be carried out in a vacuum, preferably at an absolute pressure of 1 micron of mercury or less, or in an atmosphere of argon or helium.

Gas turbine blades and vanes, coated in accordance with the present invention exhibit greatly superior corrosion and erosion resistant properties compared with uncoated blades and vanes, as well as compared with blades and vanes coated with chromium alone, or with a duplex coating of chromium and aluminum. Furthermore, blades and vanes coated by the process of the present invention are not subject to catastrophic failure after an extended period of operation, as is characteristic of many of the coated blades and vanes of the prior art.

It will be understood that the foregoing general description and the following detailed description as well are exemplary and explanatory of the invention but are not restrictive thereof.

Referring now in detail to the present preferred and illustrative process of the present invention, which will be described in connection with the coating of an otherwise finished vane of a gas turbine adapted to be operated at a temperature of 2,200° F. and even as high as 2,400° F.

The finished vane is preferably formed by forging from "TD Nickel," a dispersion-strengthened alloy composed of 98% nickel and 2% dispersed particles of thoria (ThO₂), the thoria particles being much less than 1 micron in size and substantially uniformly distributed throughout the nickel matrix.

The vane may also be formed by brazing a TDN airfoil member to a platform of TDN or other super-alloy base, such as a nickel-base super-alloy, e.g. IN-100, SM-200, Inconel 713C, SM-302, etc.

The coating mixture for the first coating to be deposited on the surfaces of the vane comprises a mixture consisting of:

	WEIGHT PERCENT		
	Range, percent	Preferred range, gr.	Optimum
Chromium powder (100 mesh or finer).....	2-98	150	17.5%, 150 grams.
Powdered alumina (Al ₂ O ₃).....	2-98	350-900	81.5%, 700 grams.
Chromic chloride anhydrous CrCl ₃	0.1-10	5-20	1.5%, 10 grams.

The optimum mixture is especially suitable for use in vacuum, or in an atmosphere of hydrogen or argon and at temperature of from 1,800° to 2,500° F. In general, at higher temperatures, the chromium content of the pack may be reduced.

These finely divided powders are thoroughly mixed for instance by being blended in a V-blender for a period of 15 minutes or more.

A glass sealed retort to receive the vane is then provided with a substantial layer of the blended powder, usually to a depth of about one inch, after which the vane is placed in the retort and covered with the blended powder, with all cavities in the vane being filled with the blended powder and areas adjacent the vane are also filled with the blended powder.

The retort is then sealed and is placed in an electrically heated muffle furnace. The muffle is then purged with argon until the oxygen content is substantially nil, after which hydrogen is added to the stream of purging argon. After a few minutes the flow of argon is stopped and the retort and furnace continue to be supplied with hydrogen for the duration of the heat treatment.

The temperature of the furnace is then raised to the diffusing temperature and held in the range of 1,800° to 2,550° F., or just below the melting point of the alloy, but preferably at about 2,400° for a period of time, usually 2 hours or more.

During the heating, the chromic chloride, or other halogen source reacts with the metallic chromium forming a metallic halide, which decomposes, causing the metallic chromium to be deposited on the surface of the vane as a thin tenaciously adherent layer. The thickness of the deposited chromium layer will vary from 0.001" to 0.003" diffused into the TD nickel to form a solid solution of chromium in nickel, or a combination of solid solutions of chromium in nickel and a solid solution of nickel in chromium, depending on processing times and temperatures.

Thereafter, the vane is to be provided with a thin, adherent layer of chromium modified nickel aluminide, and this is accomplished by treating the vane in a bed of powdered material in a retort. The powdered material comprises a mixture of the following:

	Range, percent	Preferred range, percent	Optimum grams
Chromium powder (100 mesh or finer).....	2-98	50-99	150
Aluminum powder (100 mesh or finer).....	2-98	2-50	30
which metal powders are mixed with a mixture of—			
Powdered alumina.....	2-98		700
Chromium chloride (100 mesh or finer).....	0.1-10		10

to produce a blended mixture.

The chromium-aluminum is either in the form of blended powders of chromium or aluminum or as a powdered chromium-aluminum alloy. In either case, the chromium-aluminum ratio may vary from 1 to 99% by weight to 99 to 1%, and in the pack, the chromium/aluminum content is preferably from 2 to 98% to 98 to 2% and preferably about 20% of the weight of the total pack.

5

As the concentration of metal powders in the pack is reduced, for any given temperature, the heat treatment will be extended for those packs including lower amounts of the metal powders.

The vane member is covered with a further layer of the mixed powdered material, and the retort is closed and placed within the electrically heated muffle where it is heated to a temperature in range of 1,000° to 2,550° F., preferably at 2,100° F. for a period of time, preferably about 2 hours.

At the start of the heating, the muffle containing the retort is purged with argon, until the oxygen content is substantially nil, after which hydrogen is added to the stream of purging argon. After a few minutes the flow of argon is stopped and hydrogen is supplied for the duration of the heat treatment. After the heating period has been terminated, the flow of hydrogen is continued until the vane has cooled.

There is thus provided a vane which has exceptionally advantageous oxidation and erosion resistant properties as evaluated in a gas turbine operated under test conditions.

In a similar manner, and using the procedures described above, parts formed of other alloys may be provided with a first coating of chromium, and a second coating of aluminum-chromium. The part is then heated in an atmosphere of hydrogen or inert gas, or in a high vacuum, for example at an absolute pressure of less than 1 micron of mercury, at temperatures in the neighborhood of 2,000° F. or higher for a sufficiently long period of time until the outer chromium-aluminum coating has diffused into the inner chromium coating, thereby providing a chromium-aluminum coating layer which is external to the internal chromium coating layer which is adherent on the vane or other alloy part.

While the chromium layer and chromium-aluminum layers are preferably applied to the metal part by packing the metal part in a powdered mixture of the metals with an inert filler, the coatings may be less advantageously achieved by applying the metal powders to the parts in the form of aqueous slurry, which is preferably allowed to dry on the surface of the part prior to heating the slurry-coated part to the temperature required for diffusion of the chromium or chromium-aluminum into the metal part.

Of the drawings:

FIG. 1 is a schematic sectional view of a glass sealed muffle in which a vane is packed for treatment in accordance with the present invention;

FIG. 2 is a schematic sectional view, greatly enlarged, of the protective coatings applied to the surface of a vane;

FIG. 3 is a similar view of a modified form of the coatings applied to a vane;

FIG. 4 is a graphical representation of the values obtained by actual test under similar conditions on vanes treated in accordance with the present invention, and on other specimens, with the test temperature at 2,100° F.; and

FIG. 5 is a graphical representation of the vanes obtained under actual tests of erosion at 2,200° F. showing the change in weight of a vane member treated according to the present invention and a vane member coated according to the best alternative method known to us.

Describing the drawings more in detail:

FIG. 1 of the drawing shows a retort in which the parts to be coated may be packed for coating. As shown there is provided a pan member 10 in which is seated a retort cap 12 having an open bottom side to rest against the pan member 10. The retort cap member 12 is partially filled with the packing powder 14 in an inverted position, the vane or other part 16 to be coated placed in the powder, the cap 12 is filled with powder and the pan is placed on the open bottom side after which the several parts are inverted to the position shown in FIG. 1. The edges around the cap 12 and the rim of the pan 10 are then filled with finely divided glass 18. The retort is then placed in a muf-

6

fle and is subjected to flowing argon, and then hydrogen for the duration of the heating. The glass particles are of glass which melts below the heat treatment temperature of 1,800° to 2,550° F., so that on cooling a seal is provided around the retort, thereby allowing the retort and part 16 to be cooled outside the muffle, while maintaining the part 16 in an inert atmosphere. The part 16 may then be removed by breaking the glass seal 18.

Shown in FIG. 2 is the body of a part coated in accordance with the present invention where the substrate was chromized at a rate in excess of that at which the chromium diffused into the nickel with the result that a discrete layer of alpha chromium (body centered cubic) was formed over which the aluminum-chromium blend was placed. The body of the part is formed of a dispersion-strengthened super-alloy, such as TD Nickel or other nickel base, cobalt-base or iron base alloy, and after being treated according to the present invention first with chromium metal powder and then with a mixture of chromium and aluminum powders. The innermost layer is a solid solution of aluminum and/or chromium in face centered cubic nickel over which is a layer comprising a solid solution of aluminum and/or nickel in body centered cubic chromium. The next outermost layer comprises a face centered cubic solid solution based on Ni₃Al and chromium, and the outermost layer comprises a body centered cubic solid solution based on NiAl and chromium.

FIG. 3 shows the body of a part coated in accordance with the present invention and in which the chromium was deposited on the substrate at a rate approximately equal to the diffusion rate of the chromium into the nickel with no resultant discrete chromium layer.

In this modification the innermost layer is a solid solution of chromium in nickel, the next layer is a solid solution of aluminum and nickel-chromium. The next outermost layer is Ni₃Al and chromium while the outermost layer is NiAl and chromium.

TD Nickel and related alloys are more fully disclosed in the patent to Alexander and West No. 3,180,727 granted Apr. 27, 1965.

As shown in FIG. 4, TD Nickel parts treated according to the present invention with a first coating of chromium and a second coating of aluminum-chromium, show no substantial gain or loss in weight over a long period of operation under simulated engine operating conditions, as plotted on curve A. Test temperature was 2,100° F.

Uncoated parts of TD Nickel show a substantial gain in weight which indicates a substantial degree of oxidation, resulting in eventual failure, as plotted on curve B.

Parts coated with chromium and a second coating of aluminum exhibit a large initial loss in weight, then a gradual loss in weight and an eventual catastrophic failure, as plotted on curve C.

Somewhat similarly, parts coated with a thin diffused layer of chromium, show an initially slower rate of erosion, and a more sudden catastrophic failure, as plotted on curve D.

Thus, the parts of the present invention remain substantially intact in use, without severe corrosion or erosion or oxidation, and maintain their useful life far beyond the coated parts of the prior art, and are not subject to catastrophic failure.

In FIG. 4, weight change in hundredths of a gram is plotted against time in hours.

In another test of TD Nickel alloy parts coated in accordance with the present invention were compared with similar uncoated parts of TD Nickel.

FIG. 5 is a similar group of graphs representing values obtained by actual measurement on TD Nickel parts subjected to oxidation-erosion tests at 2,200° F. In this figure, curves E and F show the weight change in centigrams plotted against time in hours. Curve E is for a part coated with a composition which is considered by us to be the best of the commercially available intermetallic coatings,

while curve F is for a coating comprising an initial layer of chromium and a subsequent outer layer of chromium-aluminum applied according to the process of the present invention.

Two TD Nickel simulated airfoils fabricated from 0.070 inch sheet stock with trailing edges welded together were tested, one coated with chromium and aluminum-chromium coatings, the other uncoated, cycled at 35 seconds hot, 25 seconds cold. The thermal shock properties of the coated specimens were almost double those for the uncoated specimens, i.e., 490 cycles vs. 280 cycles, before failure. The test temperature was 2,000° F.

Commercially coated vanes made of high strength cobalt base super-alloy in an actual engine configuration were engine tested using turbine inlet temperatures of 1,900 and 2,000° F. against vanes formed from the alloys of the present invention during which tests instrumented vanes adjacent to the vanes under test indicated that temperatures of approximately 2,300° F. were reached in the vane area.

	Turbine inlet temp.		Total time
	1,900° F.	2,000° F.	
Vane A, hrs.	71.49	40.39	139.11
Vane B, hrs.	89.69	50.76	137.4

After the vane or blade member has been treated according to the present invention it has an exterior layer of aluminum-chromium superimposed on a layer of nickel-chromium-aluminum alloy, which in turn is bonded to the base metal by a layer of nickel-aluminum-chromium. The commercially coated superalloy vanes had to be air cooled to endure these temperatures, however, the coated TD Nickel vanes endured these higher metal temperatures without air cooling.

The invention in its broader aspects is not limited to the specific steps, process and compositions shown and described but departures may be made therefrom within the scope of the accompanying claims without departure from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. A metal article resistant against damages, such as oxidation, corrosion and erosion at relatively high operating temperatures while subjected to combustion products, which comprises a dispersion strengthened nickel base alloy consisting of at least 60% nickel, enclosed within a coating consisting essentially of an innermost layer of a

solid solution of at least one member selected from the class consisting of aluminum and chromium in face centered cubic nickel, a first intermediate layer comprising a solid solution of at least one member selected from the class consisting of aluminum and nickel in body centered cubic chromium, a second intermediate layer comprising a face centered cubic solid solution of Ni₃Al and chromium, and an outermost layer comprising a body centered cubic solid solution of NiAl and chromium, the layers of said coating being bonded to each other by diffusion and the innermost layer being diffusion-bonded to said base alloy.

2. A metal article resistant against damages, such as oxidation, corrosion and erosion at relatively high operating temperatures while subject to combustion products, which comprises a dispersion strengthened nickel base alloy consisting of at least 60% nickel, enclosed within a coating consisting essentially of an innermost layer of solid solution of chromium in nickel, a first intermediate layer of a solution of aluminum and nickel-chromium, a second intermediate layer of Ni₃Al and chromium, and an outermost layer of NiAl and chromium, the layers of the coating being bonded to each other by diffusion and the innermost layer being diffusion-bonded to said base alloy.

3. The metal article according to claim 2 in which the coating has a thickness from about 0.001 inch to 0.01 inch.

4. A metal article according to claim 2 in the form of a gas turbine blade.

5. The metal article according to claim 2 in which the coating is from about 0.001 inch to 0.005 inch thick.

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

29—194, 197