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DUCTILE-CORROSION RESISTANT COATING
FOR NICKEL BASE ALLOY ARTICLES
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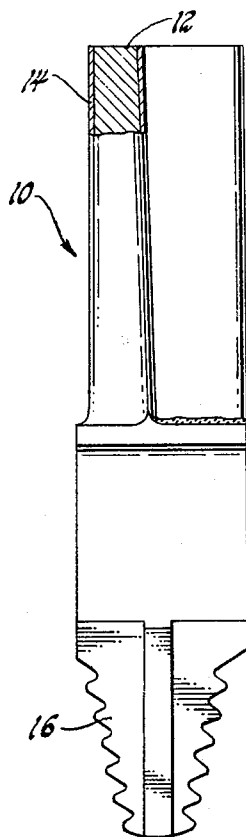


Fig. 1

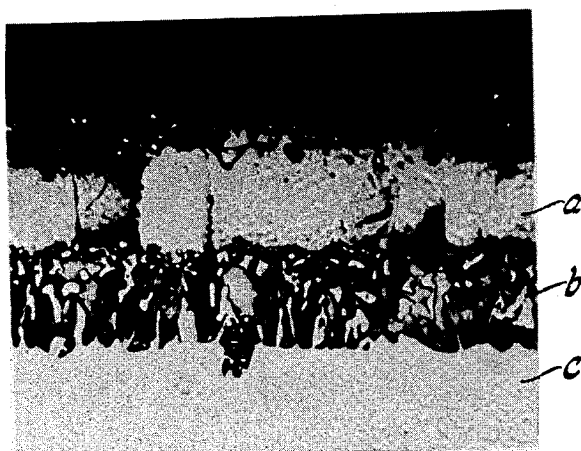


Fig. 2

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DUCTILE-CORROSION RESISTANT COATING FOR NICKEL BASE ALLOY ARTICLES

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3 Claims

ABSTRACT OF THE DISCLOSURE

Composite articles, such as turbine blades, having a nickel base superalloy core or body and a surface layer formed by diffusing aluminum, manganese and chromium into the nickel base alloy body portion, have excellent resistance to both stress rupture and corrosion at high temperatures.

The invention herein described and claimed was made under a contract or subcontract thereunder with the Department of Defense.

This invention pertains to composite materials particularly suited for use in articles, such as gas turbine engine components, which are intended to operate at high stress in corrosive, high temperature environments. More particularly, this invention relates to turbine blades formed of nickel base superalloys and having a coating layer formed by diffusing a mixture of elemental aluminum, manganese and chromium into the surface of the nickel base alloy. The resulting diffusion coating is ductile and resistant to failure under high mechanical stress as well as resistant to oxidation and sulfidation in the hot, corrosive environment of a gas turbine engine.

Designers of gas turbine engines are faced with the difficulty of finding suitable materials for use in the corrosive, high temperature environment of the first and second stages of the turbine section. As greater demands have been imposed on the output of turbine engines better materials have been sought from which the turbine blades could be formed. Turbine blades have been made using certain nickel base superalloys. These alloys maintain adequate physical strength at turbine inlet temperatures and offer some limited resistance to corrosive chemical interaction with the gaseous combustion products entering the turbine section of the engine. However, the high temperature strength of the nickel based alloys have not been fully realized because they corrode in the hot gas environment. To prevent this problem nickel base alloy blade components have been provided with coatings of materials intended to resist corrosion by the hot combustion gases. As taught in U.S. Pat. No. 3,129,069, assigned to the assignee of this invention, an aluminum diffusion coating has been employed for this purpose. The aluminum coating improved the corrosion resistance of the base alloy but proved to be too brittle for high stress applications. The coating would crack under load and expose the base alloy to the corrosive atmosphere. Diffusion coatings of other materials, such as mixtures of aluminum and chromium, and mixtures of aluminum and manganese, have also been employed. All other such materials heretofore investigated have been found to be deficient either in corrosion resistance or in resistance to stress rupture.

It is an object of the present invention to provide nickel base alloys with a diffusion coating which is resistant to both stress failure and corrosion.

It is a more specific object of the present invention to provide a turbine engine component comprising a ductile and corrosion resistant coating layer on a nickel base alloy body, the coating being formed by diffusing a combination of elemental aluminum, manganese and chromium into the nickel alloy body.

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In accordance with a preferred embodiment of our invention, these and other objects and advantages are accomplished by electrophoretically depositing a powder mixture of elemental aluminum, manganese and chromium on a surface portion of a preformed nickel base superalloy article, such as a turbine blade. Preferably the coating metals are deposited in proportions, by weight, of about 1.5 parts manganese, 1.7 parts aluminum and about 2.1 parts chromium. The base alloy and newly deposited coating are first heated in a hydrogen atmosphere at about 2000° F. for two hours. At this temperature the aluminum melts and the aluminum, manganese and chromium diffuse into the base alloy. The article is cooled in the furnace. Depending upon the composition of the base alloy, the article may then be reheated to 1500° F. or other suitable temperature in hydrogen for a suitable time to heat treat base alloy. The article is then subjected to a suitable surface cleaning treatment. Finally it is heated in air for up to about one-half hour at a temperature of 1300° F. and then air cooled. The article is then ready for use under high stress in a high temperature, corrosive atmosphere.

Other objects and advantages of our invention will become more apparent from a detailed description thereof which follows. Reference will be made to the drawings, in which:

FIG. 1 is a nickel base alloy turbine blade partly broken away and in section to show a strong, ductile corrosion resistant surface layer in accordance with this invention; and

FIG. 2 is a photomicrograph at 1000× portraying the diffusion coating and a specific nickel base alloy in accordance with this invention.

Suitable alloys for use as the base or core of composite articles in accordance with this invention are selected from the so-called nickel base superalloys. Preferably, these alloys necessarily contain, by weight, 40% to 80% nickel, 5% to 20% chromium, and may contain up to 10% molybdenum, up to 5.5% titanium, up to 6.5% aluminum, up to 3% columbium, up to 9% tantalum, up to 13.5 tungsten, up to 2% hafnium, up to 1% rhenium, up to 1.5% vanadium, up to 20% cobalt, and up to 3% iron. The nickel based alloys may also contain minor amounts of carbon, boron, zirconium, silicon and manganese. They are also likely to contain small amounts of impurities of sulfur, copper and phosphorus.

Examples of specific suitable nickel base alloys include MAR-M246 alloy (Martin Metals Company), Inconel 738 (International Nickel Company), Inconel 713C and TRW-VI A. The nominal analyses of these four alloys are summarized in the following table. It is to be expected, of course, that there will be a variation of 10% or so in the amount of each element present from the nominal value listed.

	Inconel			
	MAR-M246	738	713C	TRW-VI A
Carbon.....	0.15	0.17	.12	0.13
Manganese.....	0.10	1.0.2	-----	-----
Silicon.....	0.05	1.0.3	-----	-----
Chromium.....	9.0	16.0	12.5	6.0
Nickel.....	Bal.	Bal.	Bal.	Bal.
Cobalt.....	10.0	8.5	-----	7.5
Molybdenum.....	2.5	1.75	4.2	2.0
Tungsten.....	10.0	2.6	-----	5.8
Columbium.....	-----	0.9	2.0	0.5
Titanium.....	1.5	3.4	0.8	1.0
Aluminum.....	5.5	3.4	6.1	5.4
Boron.....	0.015	0.01	0.012	0.02
Zirconium.....	0.05	0.10	.10	0.13
Iron.....	0.15	1.0.5	-----	-----
Tantalum.....	1.5	1.75	-----	9.0
Hafnium.....	-----	-----	-----	0.4
Rhenium.....	-----	-----	-----	0.5
Copper.....	1.0.10	-----	-----	-----

¹Max.

In general, the above alloys are casting alloys and articles intended to be formed from such materials are formed by casting.

Referring particularly to the drawings, there is shown in FIG. 1 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 body portion 12 provided with a diffusion coating layer 14 initially consisting essentially of aluminum, manganese and chromium. For purposes of description the thickness of this coating layer is considerably exaggerated in FIG. 1, the actual thickness being of the order of only one to about four thousandths of an inch. It usually is unnecessary to provide the aluminum-manganese-chromium diffusion layer over the fastening portion 16 of the turbine bucket.

In general, the diffusion layer 14 is formed on a surface of a cast nickel base alloy body or core member of desired predetermined configuration. A mixture of aluminum, manganese and chromium is applied to the surface of the base alloy 10 in finely divided particulate form in a manner so as to provide an adherent layer thereof adjacent the alloy surface. The base alloy and adherent coating particles are then heated at an elevated temperature and for a time whereby the aluminum, manganese and chromium simultaneously interdiffuse with the base metal alloy to a depth of about 0.0004 to 0.006 inch to form the diffusion coating layer 14. Preferably, the diffusion heat treatment is accomplished by first heating the coated article at about 1300° F. for about one hour and subsequently heating the article for about two hours at about 2000° to 2100° F. in a hydrogen environment.

Several methods for simultaneously diffusing the aluminum, manganese and chromium into the base metal are suitable for forming a ductile and corrosion resistant surface.

Preferably, an initial coating of powdered aluminum, manganese and chromium is provided on the nickel base alloy article by electrophoretic deposition. Electrophoretic deposition involves applying a mixture of aluminum, manganese and chromium particles to the nickel base alloy article by first suspending the particles in an organic, dielectric solvent. The article to be coated is immersed in the suspension and adapted as the cathode in a direct current electrical circuit. When subjected to a potential of 50 to 500 volts the metal particles in the suspension are caused to deposit in a layer of uniform thickness on the cathodic nickel base article. Subsequently the coated article is heat treated to diffuse the metal particles into the base layer.

A bath for the electrophoretic codeposition of aluminum, manganese and chromium was prepared as follows. A quantity of a solvent mixture consisting of 60% $\pm$ 5% by weight isopropyl alcohol and 40% $\pm$ 5% by weight nitromethane was first prepared. Two grams of cobalt nitrate hexahydrate were then dissolved in a liter of these mixed solvents to make up a first solution—solution A. A second solution—solution B—was prepared by dissolving 10.8 grams zein in a liter of the same mixed solvents.

Two hundred milliliters of a bath solution suitable for electrophoretic deposition were then made up by mixing 10 milliliters of solution A, 50 milliliters of solution B and 140 milliliters of the above isopropyl alcohol-nitromethane mixed solvents. To this bath solution were added 1.7 grams of aluminum powder of less than ten micron particle size, 1.5 grams manganese powder of less than ten micron particle size, and 2.1 grams of chromium powder having an average particle size of about one micron. The metal particles and solution were thoroughly mixed in a blender. The resulting suspension was placed in a beaker and the suspension was maintained by mild agitation.

A turbine bucket cast from MAR-M246 nickel base

alloy was immersed in the suspension. It was adapted in a direct current electrical circuit to function as a cathode. A nickel strip shaped to fit closely about the turbine bucket was adapted as an anode and immersed in the bath adjacent the blade. A direct current potential of 200 volts was applied between the cathodic turbine blade and the anode for one minute at room temperature. During this period the three metals were codeposited in powder form upon the turbine blade. A small amount of the zein was deposited with the metals and it appeared to function as a binder and an electrical insulator. The thickness of the green coating was found to be about 17.0 mils.

The coated blade was air dried to evaporate residual solvent and subsequently placed in a hydrogen atmosphere furnace, initially at room temperature. The furnace was heated to 1350° F. and maintained at this temperature for one hour. Volatile and decomposable materials, such as zein and residual solvent, were removed from the coating and the aluminum was melted. The MAR-M246 bucket and coating were then heated in a hydrogen atmosphere at 2000° F. for two hours. Following the two hour period the blade was rapidly cooled in the furnace by purging with cool hydrogen. The coated MAR-M246 turbine bucket was then reheated to 1500° F. for fifty hours to heat treat the base alloy.

The composite turbine bucket was then removed from the furnace. The surface was cleaned by blasting with No. 240 alumina grit at 17 p.s.i.g. air pressure. Some loose, powdery material was removed from the surface of the blade. The clean blade with its diffusion coating was then reheated in the furnace at 1300 $\pm$ 25° F. for about twenty minutes in air. The blade was then air cooled.

The photomicrograph of FIG. 2 depicts the diffusion coating and the adjoining MAR-M246 alloy of a turbine bucket in accordance with our invention at this stage of processing. The diffusion coating is about 1.5 mils in thickness.

An electron microprobe analysis revealed the following information with respect to the chemical content of the subject coating at the completion of the interdiffusion of the electrophoretically applied layer and the base MAR-M246 alloy. Reference is made to FIG. 2.

Zone A is rich in Al, Co, Cr, and Mn with lesser amounts of Ni and W.

Zone B is rich in Co, Al, and Cr with lesser amounts of Mn, Ni, and W.

Zone C is the MAR-M246 base material plus diffused Mn.

The B to C interface is rich in W, Co, and Cr along with other base material elements.

A qualitative X-ray diffraction analysis of the surface of the coated blade detected the presence of relatively major amounts of elemental aluminum, nickel, and chromium and of the intermetallic compound NiAl. Relatively minor amounts of elemental manganese and cobalt and of the intermetallic compounds of Al₅Cr and AlCo were also detected.

It would be expected that some minor chemical differences would be detected when the subject diffusion coating is formed on other nickel base alloys due to differences in the compositions of the base alloys. Nevertheless the resultant coating on these suitable nickel base alloys is still highly ductile and corrosion resistant.

In accordance with our invention, it is preferred that the proportions of aluminum, manganese and chromium in the initial electrophoretic coating, prior to the diffusion heat treatment, be maintained within about $\pm$ 10% of the proportions set forth in the above example. In other words, about 1.3 to 1.7 parts by weight of manganese, about 1.5 to 1.9 parts of aluminum and about 1.9 to 2.3 parts chromium are employed. Taking one part of manganese as a basis, the proportion of aluminum may be about

0.85 to 1.45 and the proportions of chromium about 1.1 to 1.75.

The concentrations of these materials in the coating bath may be varied somewhat to achieve a thicker or heavier green coating as desired. For example, we have found that when about 1.5 grams of aluminum powder are employed in 200 milliliters of the electrophoretic vehicle of the above example, the resulting electrophoretic coating is about 1.5 mils thick after one minute of deposition. When 1.7 grams of aluminum powder were employed per 200 milliliters of vehicle, the resulting electrophoretic coating was about 1.7 mils thick after one minute of deposition. While the electrophoretic deposition is suitably carried out in a period of about one minute, considerable variation in deposition time and deposition voltage can be had and still obtain a suitable coating. The zein, which is codeposited with the metals, acts as an electrical insulator. It thereby promotes coatings of uniform thickness and tends to limit the ultimate thickness of the coating.

The ultimate diffusion coating should be in the range of about four-tenths of a mil to six mils in thickness. When the coating is formed to turbine components, preferably a coating of about 2.5 to 3 mils is obtained on vanes and a coating thickness of about 1.5 to 2 mils on the thin walled, hollow blades.

Composite turbine blades in accordance with the invention have excellent physical properties, particularly at the relatively high temperatures encountered in the gas turbine. The subject diffusion coatings are quite ductile and resistant to stress rupture and spalling. They are also quite resistant to corrosion such as oxidation and sulfidation. For example, a number of the MAR-M246 blades having the subject aluminum-chromium-manganese diffusion coating were found to have an average ambient tensile strength of 115,000 p.s.i. The properties of the composite material at temperatures of about 1400° to 1900° F. are more important, however, in evaluating its utility in a gas turbine. When a number of the MAR-M246 test specimens with the subject diffusion coating were subjected to a constant stress of 20,000 p.s.i. at 1800° F., they were found to have an average rupture life of 117 hours. When another group of like specimens were subjected to a stress of 65,000 p.s.i. at 1450° F., they were found to have an average rupture life of 221 hours. Another group of like test specimens were maintained at a temperature of 2050° F. and subjected to a cyclically applied load up to 10,500 p.s.i. tensile stress. It was found that these test specimens withstood an average number of 2840 cycles before failing under these conditions.

A number of test specimens consisting of MAR-M246 base alloy were prepared with a commercial diffusion coating of chromium and aluminum. Groups of these test specimens were subjected to the same set of tests described above. The average rupture life of this composite material at 1800° F. under a constant stress of 20,000 p.s.i. was 62.4 hours. The average rupture life at 1450° F. and 65,000 p.s.i. was 60.7 hours. A group of these coated specimens withstood an average of only 1527 cycles at 2050° F. under a cyclically applied load of up to 10,500 p.s.i. tensile stress. It is seen that MAR-M246 specimens provided with an aluminum-manganese-chromium diffusion coating withstand stresses at elevated temperatures to a markedly greater degree than do specimens formed of the same base alloy and having a commercial aluminum-chromium diffusion coating.

Turbine blades of MAR-M246 base alloy with the subject aluminum, manganese and chromium were subjected to a hot corrosion test at temperatures up to 1900° F. in a spray of sodium sulfate. The blades were mounted on a rotating fixture which continually moved them into and out of a 1900° F. furnace and through the spray of corrosive material. Six blades sustained an average of 562 cycles before the coating failed. By way of comparison, the commercial aluminum-chromium coating on the same base

alloy sustained only an average of 377 cycles before failure.

The subject coating when applied to the TRW-VI A nickel base alloy sustained an average of over 900 hot corrosion test cycles before coating failure, whereas aluminum-manganese coatings over the same base alloy survived less than 400 cycles before coating failure, and aluminum-chromium coatings over the same base alloy survived only 500 hot corrosion test cycles before the coating failed. Therefore, it is seen that the subject coating is highly stress resistant at elevated temperatures and is resistant to oxidation, sulfidation and other forms of corrosion in environments typically found in the gas turbine engine department.

As indicated above, it is preferred that the aluminum-manganese-chromium mixture be initially applied to the nickel base alloy article by electrophoretic deposition. It is an economical, reproducible process which can be carried out at ambient temperatures. However, it is to be realized that a diffusion coating can also be obtained, for example, by the packed diffusion process. In this method the nickel base article to be diffusion coated is packed in a retort surrounded by a suitable powdered mixture consisting of the metals to be diffused and an activator carrier. The article is then heated in the retort and subsequently in a hydrogen environment to obtain a diffusion coating. In accordance with our invention the nickel based alloy would be packed in a powder mixture containing, for example, aluminum powder, manganese powder, chromium powder, a small amount of ammonium chloride and aluminum oxide. Preferably the powders are of five micron size or smaller. The powder composition is placed in a retort with a turbine blade specimen and the packed retort is heated in the furnace to about 1350° F. for one hour. The blade is then cooled in the retort to a handling temperature. It is then removed from the retort and placed in a hydrogen atmosphere furnace to complete the diffusion in accordance with the procedure of the above example.

It is also possible to suspend aluminum, manganese and chromium powders in an inorganic liquid binder and apply the suspension to surfaces of the article to be coated by dipping or spraying. After drying the coating the article is heat treated to obtain a diffused coating.

In the electrophoretic deposition procedure described above a mixture of aluminum, manganese and chromium powders in suitable proportions was prepared. It will be appreciated that an alloy in powder form of these materials can also be employed.

Although the invention has been described in terms of certain specific embodiments, it is to be understood that other forms may be adopted in the scope of the invention.

What is claimed is:

1. A strong corrosion resistant article for use in a high temperature environment, said article being formed of a nickel based alloy having diffused in the surface of at least a portion thereof the combination consisting initially by weight of about one part manganese, 0.85 to 1.45 parts aluminum, and 1.1 to 1.75 parts chromium to form a diffusion layer of about 0.4 to 6 mils in thickness,

said nickel based alloy consisting essentially on a weight basis of 40% to 80% nickel, 5% to 20% chromium, up to 10% molybdenum, up to 5.5% titanium, up to 6.5% aluminum, up to 3% columbium, up to 9% tantalum, up to 13.5% tungsten, up to 2% hafnium, up to 1% rhenium, up to 1.5% vanadium, up to 20% cobalt, up to 3% iron, and minor amounts of carbon, boron, zirconium, silicon and manganese.

2. A turbine blade formed of a cast nickel based alloy and having a diffusion coating about 0.4 to 6 mils in thickness on a surface of said nickel alloy, said coating being the interdiffusion product of said nickel alloy and a combination of metals consisting essentially of one part manganese, about 0.85 to 1.45 parts aluminum and about 1.1 to 1.75 parts chromium,

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said nickel based alloy consisting essentially on a weight basis of 40% to 80% nickel, 5% to 20% chromium, up to 10% molybdenum, up to 5.5% titanium, up to 6.5% aluminum, up to 3% columbium, up to 9% tantalum, up to 13.5% tungsten, up to 2% hafnium, up to 1% rhenium, up to 1.5% vanadium, up to 20% cobalt, up to 3% iron, and minor amounts of carbon, boron, zirconium, silicon and manganese.

3. A turbine blade formed of a cast nickel based alloy and having a diffusion coating about 0.4 to 6 mils in thickness on a surface of said nickel alloy, said coating being the interdiffusion product of said nickel alloy and a combination of metals consisting essentially of one part manganese, about 0.85 to 1.45 parts aluminum and about 1.1 to 1.75 parts chromium.

said nickel based alloy having the nominal composition by weight of 0.15% carbon, 0.10% manganese, 0.05%

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silicon, 9.0% chromium, 10.0% cobalt, 2.5% molybdenum, 10.0% tungsten, 1.5% titanium, 5.5% aluminum, 0.015% boron, 0.05% zirconium, 0.15% iron, 1.5% tantalum, 0.10% maximum copper and the balance nickel.

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