Feb. 3, 1970 J. G. LUCAS ET AL 3,493,476

SULFIDATION AND OXIDATION RESISTANT COATING

Filed Nov. 1, 1965 2 Sheets-Sheet 1

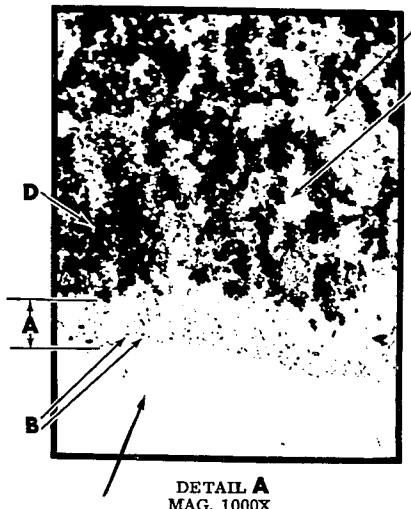


FIG. 2

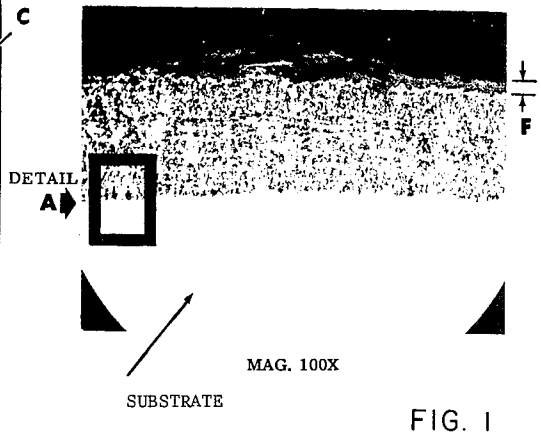


FIG. 1

COMPOSITION - WEIGHT PERCENT

AREA	DESCRIPTION	Ti	Fe	Cr	Al	Ni	S	Mo	Cb
A	DEPLETED ZONE	0.1	0.9	2.9	1.7	91.0	-	3.2	0.1
B	Cr_xS_y PHASE	4.1	0.5	47.5	2.9	-	41.2	-	4.1
C	UNATTACKED METAL	0.02	0.9	1.4	1.2	93.3	-	2.2	0.9
D	OXIDE MATRIX	2-3	0.4	17-19	14-16	17-19	-	1-2	1-2
E	INTERNAL OXIDATION	0.2	0.9	3.4	5.8	84.2	0.1	5.8	0.1
F	UNIFORM SCALE LAYER	0.5	1-2	8-9	4-5	66-68	-	0.2	2-3
	NOMINAL COMPOSITION	0.75	0.5 max.	13.0	6.00	Bal.	0.015 max.	4.5	2.3

Characteristics of Sulfidation Attack in an Engine-Operated Turbine Nozzle Vane

FIG. 3

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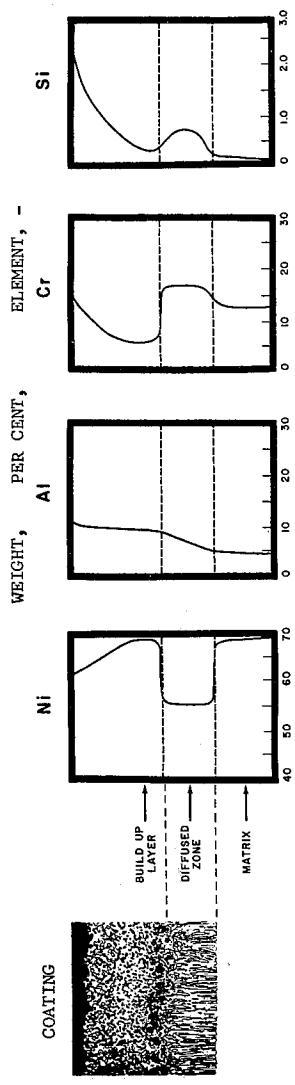


FIG. 4

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SULFIDATION AND OXIDATION RESISTANT COATING

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ABSTRACT OF THE DISCLOSURE

A method of producing a sulfidation and oxidation resistant coating upon nickel base alloys wherein chromium and aluminum-silicon layers are imposed upon the base and then subjected to such temperatures as will cause diffusion of these layers, resulting in a product wherein the base material is provided with a chromium rich intermediate layer and an aluminum rich exterior layer.

This invention relates to a method or a coating of nickel base alloy parts to render the same not only resistant to oxidation, but also, extremely resistant to sulfidation by reason of sulfur attack in hot corrosive atmospheres.

This problem of corrosive deterioration by reason of oxidation or sulfidation of alloy substrate materials is one of crucial significance in at least one vital area—manufacture or parts or components of turbines commonly used in the propulsion systems of jet aircraft. Breakdown by reason of excessive erosion or corrosion over minimum periods of time through the influence of either oxidizing or sulfidizing phenomena occurs particularly in vanes or buckets which are made of nickel base alloys of extreme strength. The vane elements, of course, are exposed to extreme temperatures; also to highly corosive atmospheres, and further, since these comprise the power producing components of the turbine, they nevertheless should necessarily exhibit the greatest resistance to deterioration of the types mentioned.

Much effort has heretofore been aimed at, particularly, varous means or modes of processing to inhibit or retard the oxidation of nickel base alloy component parts. Freeman and Lucas Patent No. 3,155,536 presented a solution to the one factor mentioned—that of retarding or substantially preventing oxidation, at least over a period of time that would extend the operational life of a given turbine to a reasonable number of hours. Such patent is directed to a system wherein by a deposition or alloying reaction the substrate material is provided with an aluminum or aluminum alloy surface, closely bonded to or alloyed with the nickel base substrate. This system, as indicated, does effectively, by the provision of such an aluminum surface component, reduce oxidation attack to levels consistent with aircraft performance at least to the extent that turbine replacement or repair is not required for a reasonable number of hours of flight operation.

It has been found, however, that there remains an additional factor substantially reducing the life of blade components to a point where repair or replacement of the blades is indicated after only as little as 300 hours of operation. We have found that despite the effectiveness of the oxidation resistant treatment, as outlined in the aforesaid Freeman and Lucas patent, another corrosive influence is at work, the latter being somewhat unrelated to erosion through oxidizing reactions. It further appears that this heretofore unappreciated type of attack upon alloys of the described nature, operating at reasonable high temperatures (1450° F.) is particularly frequent

with respect to aircraft operating on or near salt water areas of the earth's surface. It has thus been determined that the natural sodium sulfate of sea water forms a sulfide penetration into the substrate material, and it is this resultant effect the instant invention inhibits or precludes. The remaining native magnesium chloride, sodium chloride, and other halides and salts of natural sea water would appear to perform as moderate catalytic reagents accelerating the formation of the sulfide surface or, differently stated, the sulfidation of the exterior and terminal portions of the blades in turbine propulsion systems. Such has, in many instances, so deteriorated the operational life of turbines operating in sea areas that either frequent overhaul or frequent replacement of the blades and/or turbines is necessary. By frequent is meant replacement within only from 300 to 700 hours of operation when the aircraft should normally function with relative efficiency over a period of time of at least 2,500 hours.

The instant invention is the provision of a method of treatment of a nickel base alloy component in such manner as to provide a chromium rich alloy layer intermediate the substrate and the final oxidation-resistant layer, the latter being of an aluminum-silicon type.

The solution to the problem is not as obvious as simply increasing the chromium content of the substrate, it being recognized that chromium per se is relatively immune to attack from sulfidation. This is because the ideal nickel alloy substrate must be one meeting the requirements of internal strength demanded in the turbine components of a given prolulsion system. Maximum strength of a nickel alloy substrate for the desired objectives is found in an alloy containing no more than 10% of chromium. If such substrate is an alloy containing more than 16% of chromium, then perhaps the problem of sulfidation has been resolved, but this only at a sacrifice of reducing the strength of that nickel alloy substrate. We have approached the problem from this viewpoint: Providing a substrate of maximum strength for the desired purposes, i.e., a nickel alloy base material having, preferably, up to 10% chromium. This percentage of chromium, however, is present in an insufficient amount to thwart substantial sulfidation. Therefore, we, as indicated, provide an intermediate layer between the substrate and the aluminum-silicon outer layer, which intermediate layer by its substantially larger percentage of chromium content, does withstand attack through the sulfidation phenomenon. At the same time the outer alloyed aluminum layer—preferably an aluminum-silicon aloy—resists attack through oxidizing influences. Hence, the instant process revolves about the basic and novel concept of a duplex sulfidation-oxidation resistant overlay, increasing the life of such components in the case of turbine propulsion systems to a reasonable one—a longevity in flight hours of operation of 2,500 hours or more, even though the aircraft is operating in sea areas where sulfide formation would normally reduce operational efficiency to not only an uneconomical but dangerous level.

It is, therefore, a primary objective of the instant invntion to provide a method of treatment of component parts, particularly those used in gas turbine propulsion systems for aircraft, which results in such parts exhibiting not only anti-oxidation characteristics but extreme resistance to sulfidation as well.

It is another object of the invention to provide a method of the described type for the treatment of primary nickel base alloy materials of maximum internal strength due to the inclusion in the substrate of no more than about 10% chromium, such method involving incorporation of an intermediate fused layer or zone rich in chromium and, hence, extremely resistant to the catalyzed attack of the sulfates, particularly sodium sulfate, found in salt

water. It is here to be appreciated that a range of from 10% to 15% chromium inclusion is permissible, dependent upon the specific nature of the nickel base alloy used in fabrication of the particular component.

It is a further object of the invention to provide a system of nickel alloy matrix treatment wherein additions of chromium and aluminum-silicon alloy are applied to the surface of the substrate in layers, rather than as a mixture. This results in an intermediate diffusion zone much higher in chromium content, the latter thus forming a semi-continuous chromium rich barrier which inhibits co-diffusion of the aluminum or aluminum-silicon outer layer inward, and the substrate elements outward.

It is another object of the invention to provide a nickel base treated method where such substrate is of maximum strength due to the stated limitations as to chromium inclusion, but such substrate is protected from the adverse effects of sulfidation by a fused intermediate layer, the latter being rich in that natural component (chromium) which is normally not subject to attack by sulfide formation as is the case of a base alloy having, for example, a high percentage of nickel content but only about 10% chromium.

It is a further objective of the invention to provide a sulfidation resistant coating or zone as an intermediate layer between the substrate and an outer oxidation resistant layer or zone, the latter being applied through the procedures described in the aforesaid Patent No. 3,155,536, as the result of which an even final aluminum-silicon layer, is evenly and effectively applied, such layer actually being alloyed with the referred to chromium rich intermediate layer. In this respect there is a significant difference between the instant procedure and that of the said patent in that, as indicated, the final anti-oxidant coating comprises an alloy of aluminum and silicon in the preferred respective percentages by weight of 88% and 12%.

The following further description of the invention is made with respect to certain photomicrographs, used in conjunction wiht accompanying charts for explanatory purposes, and wherein:

FIGURE 1 is a reproduction of a photomicrograph taken at 100 magnification showing a cross section of a typical nickel base alloy, untreated by the method of the invention, which has undergone the corrosive effects of sulfidation;

FIGURE 2 is a reproduction of a photomicrograph taken at 1,000 magnification and comprising an enlargement of Detail A of FIGURE 1;

FIGURE 3 is a chart explaining the various areas of deterioration at the surface of the article indicating the amounts of the individual elements present at various levels in the cross sections of FIGURES 1 and 2; and

FIGURE 4 is a reproduction of the photomicrograph of one typical nickel base alloy treated in accordance with the present invention, accompanied by a series of four graphs indicating the percentage amounts of each of the elements nickel, aluminum, chromium and silicon in each of three layers—the substrate or matrix, the diffused zone and the buildup or outer aluminum-silicon rich layers.

As indicated, the invention is particularly applicable to the treatment of turbine blades such as the gas producer turbine blades of modern jet propulsion systems. A typical blade is illustrated in the Freeman and Lucas Patent No. 3,155,536. Such are designed to operate at temperatures of about 1600° F. and, of course, under extreme corrosive conditions. Once the pressure surfaces of such a blade are attacked or corroded through the deteriorative action of either oxidation or sulfidation, or both, the blade proportionately loses its pressure effect until it becomes most inefficient and finally, when the cross sectional area is reduced at points of high stress, premature in extreme cases, fracture of the blade may follow, thus requiring replacement.

It is evident that an infinite number of base alloys are available but metallurgical science dictates the production, at least for the purpose of manufacture of turbine blades, of a base metal that is extremely wear resistant, of great hot strength, durable and, of course, inherently resistant to ordinary corrosive deterioration to the best degree possible. As typical of base or substrate alloys which are here contemplated as being useful in the fabrication of e.g. gas producer turbine blades, the following table sets forth a series of five alloys, characteristically identified as nickel base alloys because of the preponderance of that element in each of them.

TABLE 1

	Nominal chemistry of typical commerical high temperature turbine alloys (amounts in percentages by weight)										
Alloy	Cr	Al	Ti	Mo	Cb	Ta	Co	W	V	C	Ni
A	13.00	5.75	0.75	4.50	2.0					0.14	72.0
B	10.00	5.50	5.00	3.00			15.0		1.00	0.18	59.8
C	9.00	5.00	2.00		1.0		10.0	12.5		0.15	59.8
D	10.00	6.50	1.0	4.00	1.0	2.0		2.0		0.18	73.2
E	8.00	6.00	1.0	6.00		4.0	10.0			0.10	64.1

It will be noted with respect to the foregoing table that alloys are here preferred which do not exceed a chromium content of more than 13%, and as a matter of fact, a 10% inclusion, as in alloys B and D, is preferred. This lower percentage of chromium is conductive to obtaining an alloy, in conjunction with the other components as indicated, of extreme strength and durability. Were it possible to include a chromium content in the alloy of, for example, 35% then this base material would inherently be resistive to sulfur sponsored corrosive activity consequent upon the presence, in the operating atmosphere of the turbine of such sulfates as, primarily, sodium sulfate. However, to increase the chromium component in such an amount as to resist sulfide formation produces an ultimate base material far too weak to meet other strength requirements under the high temperature conditions which exist in gas producer turbines during normal operation.

As the table indicates, such nickel content of this type of base alloy varies from about 64% to 72% and each of the alloys A to E further differs in the inclusion of different minor metals and in their respective percentages in the alloy. All are characteristic in this one regard—that all contain a substantial amount of aluminum, around .15% of carbon, from 1 to .75 of titanium, and all, except alloy C, from 3 to 6% of molybdenum.

The corrosion problems with which we are here concerned are illustrated in the photomicrographs of FIGURES 1 and 2. These illustrate the results of sulfidation with respect to a typical nickel base alloy. Here it is seen that there are actually what might be termed four layers: The substrate itself comprising the nickel alloy base materials, opposite that an exterior zone F of total oxidation, and in between two additional sections. The latter comprise the depleted zone A or what might roughly be termed a zone of internal and incomplete sulfidation. In this depleted zone A the percentages indicated in FIGURE 3 strikingly illustrate deterioration by sulfidation of, as here shown, an untreated nickel alloy material. Whereas the base alloy contains 13% chromium, in such depleted zone, and after sulfur attack, the chromium content has been reduced to 2.9% with the chromium now

in the form of chromium sulfide, the latter having a chromium content of 47.5% and a sulfur content of 41.2%. This chromium sulfide phase is indicated at B, the grey areas representing the sulfide and it being noted, again, that the sulfidation process is taking place underneath the partially oxidized layer.

This latter layer is comprised of an oxide matrix D within which the light areas C indicate the as yet unattacked metal (non-oxidized) with the grey areas E in such latter area C indicating internal oxidation.

The zone A, or depleted zone, is one consisting predominately of the nickel component, as indicated, with a low chromium content of 2.9%, and as further indicated, a very high chromium sulfide percentage. It is the latter phase, of course, which represents the deteriorative consequence of sulfidation.

In summary, the main distinguishing characteristic of this form of sulfidation corrosion is the zone A which is developed at the oxide/base metal interface in which an extraneous light grey phase B is formed. Proceeding outward from this zone is a mixed inner scale layer composed of areas of "unattacked" metal C dispersed in an oxide matrix D; finely dispersed particles E are visible in the unattacked metal areas of this inner scale. Finally, at the outer surface of the corroded part is a layer F of complete oxidation.

The zone developed along the metal/oxide interface is clearly an alloy depleted area relative to the original alloy's composition, being approximately 91.0% Ni with small amounts of chromium, aluminum, and molybdenum present. The extraneous light grey phase represents a chromium sulfide precipitate which is best approximated by the stochiometric phase Cr_3S_4 with small amounts of titanium, aluminum, and columbium in solid solution. The formation of this phase is obviously dependent on sulfur adsorption from the atmosphere and results in a severely localized concentration of the alloy's chromium content similar to sensitization in stainless steels. The resultant low chromium and aluminum contents in the surrounding matrix A are also apparent from the complete lack of gamma prime, Ni_3 (Al, Ti), in this area. The results of analysis of the unattacked metal areas dispersed in the inner scale layer indicate they are similar in composition to the depleted matrix. The composition of the metal oxide areas in the inner scale and outer scale layer, together with X-ray diffraction analysis of the bulk scale, indicates these areas are predominately composed of the spinels, $NiCr_2O_4$ and $NiAl_2O_4$ (inner scale layer) and NiO (uniform outer scale layer). The analysis of the finely dispersed particles in the unattacked metal area of the inner scale is not considered representative of their actual composition. It is reasonable to suspect that these particles are the start of internal oxidation of these metal islands.

The photomicrographs of FIGURES 1 and 2 were taken of an untreated nickel alloy base material (in the form of a turbine nozzle vane) subjected to an environment of synthetic see water. Salt residues from such a solution exposure consisted of 7.9% sodium sulfate and 51.7% sodium chloride.

The preferred solution is typified by the ASTM specifications for synthetic sea water. This appears in ASTM Specifications D665–60, ASTM Standards A61, part 7, page 312, procedure B.

Such breakdown of the surface was obtained with respect to an untreated piece by operation of a conventional gas turbine for a period of 120 hours at 1600° F. The contaminant, in the form of such synthetic sea water, as above, was injected into the intake air at a constant rate of four parts per million parts of intake air. The resultant deterioration, through sulfidation, and as indicated in the photomicrographs of FIGURES 1 and 2 is the deciding factor as to life of the component, it being determined, as indicated above, that less than 200 hours of operation at the stated temperature, or temperatures in that neighborhood, render the vane or bucket component either most inefficient or completely inoperative.

With regard to the sulfidation phenomena, it is hypothesized that the attack is initiated by destruction of the normally protective oxides which form on the alloy surface, i.e. the surface of the alloy in contact with the environment. Reaction of the exposed base material with the environment follows, producing sulfur absorption by the alloy surface. Restoration of the protective chromium rich oxide is thereby hindered due to a chromium-sulfur reaction and the formation of a chromium rich sulfide internally in the base metal and here indicated as depleted zone A which has thickly interspersed throughout it the chromium sulfide phase B.

The second phase of the sulfidation reaction can proceed rapidly once the internal strength of the outside form, as breakdown of the protective scale, has been started. It is possible that this phase of the corrosion process occurs at the metal scale interface where chromium from the alloy reduces the sulfur gases, producing a chemically reducing micro-environment locally within the scale. Thus, although the bulk of atmospheric conditions in the turbine section are strongly oxidizing (with an air to fuel ratio in excess of 50 to 1) such sulfur attack takes place locally at the metal-porous scale interface. In any event, it would appear that sulfur produced by reaction with chromium or the nickel base solid solution is oxidized at the metal surface following disruption of the protective oxidized film.

The problem, particularly with respect to nickel base alloys, may also possibly be explained in this fashion: That the internal diffusion of sulfur may result in the formation of both chromium sulfide and nickel sulfide, the latter forming an eutectic with nickel ($Ni+Ni_3S_2$) which is liquid about 1193° F. or at a temperature substantially below that of the normal operating temperatures of propulsion systems herein contemplated (1600° F.).

In summary, then, our novel concept includes recognition of the basic problem—that nickel base alloys, although even treated to become oxidation resistant in the manner taught in the aforesaid Freeman and Lucas patent, are not sufficiently resistant to sulfidation attack when subjected to sea water atmospheres at the high temperatures which gas turbine operation involves. At the involved relatively high temperatures in such an environment, salts of sodium sulfate, aided in some measure by other halide salts as sodium chloride, aggressively attack these nickel base alloys even if such have been protected against ordinary oxidizing reactions by a fused layer of aluminum or aluminum alloy. While it is appreciated that increasing the chromium content of such nickel base alloys would increase resistance to sulfidation, this increase in chromium content reduces the rupture like of the component. Accordingly, the problem has been resolved, not by increasing the amount of chromium in the substrate alloy but by providing a chromium-rich interface, thereby preserving the rupture strength which is characteristic of nickel base alloys having a chromium content of not substantially more than 10%, and in all cases not exceeding 15%.

In accordance with the instant invention, it will be observed that chromium and aluminum-silicon are applied in layers, rather than as a mixture as might be characteristic of the pack-cementation process. The result is provision of a broader diffusion zone, much higher in chromium content, which forms a semi-continuous chromium-rich barrier that inhibits co-diffusion of the aluminum or aluminum-silicon outer layer inward and the substrate element outward.

It has also been found that the aluminum coating or layer is far more effective, insofar as increased oxidation resistance be concerned, if such outer layer consist of an aluminum alloy having a 12% inclusion of silicon (i.e., 88% aluminum). Silicon addition in the amount stated further substantially increases the oxidation and sulfication resistance of this overlay.

The initial step in preparation of the surface of the

nickel alloy substrate is the cleaning of the surface preparatory to chrome plating. Preferably this is done by a dry abrasive blast using silicon carbide or aluminum oxide of 220 mesh size and at an air pressure of 90 to 100 p.s.i.

Such is followed by an additional wet abrasive blast utilizing aluminum oxide of finer mesh (325), the oxide being in suspension in water in the proportion of 3 pounds of abrasive per gallon of water, the air pressure being between 30 to 60 p.s.i.

The piece is then treated with a 15 to 20% hydrofluoric acid solution, at room temperature, and this followed by treatment with a 15 to 20% hydrochloric acid pickle solution, again at room temperature. These steps prepare the nickel alloy element for chrome plating.

Although the so-called pack process for chrome deposition may be used, we have found chromium electro plating to effectively deposit the chrome layer. As practiced, a usual and standard chrome solution may be used. An effective chromium plate of between about 0.001–0.0005 inch plate thickness is sufficient for the described purposes. The piece should then be rinsed in cold water and air blast dried.

Following such chromium plating to the indicated extent the nickel alloy base material is then provided with a protective oxidation resistant layer. Before dipping in an aluminum or preferably, an aluminum-silicon bath for this purpose the chrome plate article can be subjected to treatment in a fluxing bath of the same nature as that described in the aforesaid Freeman and Lucas Patent No. 3,155,536. As there explained, the fluxing bath is one preferably consisting of molten neutral salts of potassium chloride and sodium chloride, such having added thereto aluminum fluoride and cryolite, the latter for the purposes described in the said patent. The other steps involved in the fluxing procedure are to be followed as set forth in this patent and the descriptive portions of same with reference to these procedures are incorporated herein by reference thereto.

The piece is now ready for subjection to the aluminum or aluminum-silicon alloy bath. Here, again, the steps described as to dipping in molten aluminum—the time and temperature gradients to be followed, etc., are prescribed in the aforesaid patent, then post dipping the parts into the molten flux bath maintained at about 1400° F. for up to 30 seconds to attain salt bath temperature and establish the initial diffused alloy layer.

Unalloyed aluminum may be used as the protective oxidation resistant coating. However, an alloy is preferred and in this case, a 12% inclusion of silicon is preferred, thus producing a protective layer comprising an alloy of 88% aluminum, 12% silicon, although lesser amounts of silicon, as from 1% to 12%, may be employed. Such addition of silicon, particularly with reference to its 12% inclusion, is significant in that the result is to substantially increase the alloy's resistance to oxidation and sulfidation.

Whether the exterior layer be aluminum or an aluminum alloy, the same procedure with respect to the removal of an excessive overlay of aluminum is utilized as that described in the aforesaid Freeman and Lucas patent. In other words, after removal from the melt the coated parts are subjected to a whip or other type of agitation to remove a substantial portion of the excess of the aluminum-silicon alloy. When cooled, washer, etc., the excessive aluminum-silicon layer is removed by the replacement reaction described in the aforesaid Freeman and Lucas patent. As therein set forth, nickel chloride is reacted with such "excess" of aluminum-silicon alloy resulting in the replacement of such excess with nickel metal. The latter is then reacted with nitric acid, this inorganic acid removing such nickel and leaving as a chromium-aluminum-silicon layer a smooth, even coating which is actually bonded to, or alloyed with, the underlying chromium layer.

The above procedure is followed by further diffusion of the chromium-aluminum-silicon layers as the result of heating the piece to a temperature of between 1975° F. and 2050° F. Too high a temperature, as, for example, 2150° F., results in an excessive diffusion of chromium with resultant lowering of the high temperature strength of the base alloy. Temperatures substantially lower than that indicated will not, of course, produce the necessary diffusion of the chromium and aluminum-silicon layers.

The diffusion step is followed by other elevated temperature treatments for the purpose of aging the base alloy. Such later aging procedures have no effect upon the diffused chromium and the aluminum-silicon coatings since they have already been diffused at a higher temperature. The aging or precipitation to one degree or another of the various elements found in the base alloy to cause the latter to exhibit the necessary requirements of rupture and tensile strength, etc., are procedures known to the art and not particularly relevant to the instant invention, except for the point made above—that because of the high temperature gradient at which diffusion of the layers is performed, subsequent aging treatments have no effect upon these oxidation and sulfidation resistant layers, since performed at substantially lower temperatures.

Actual tests have proved the utter effectiveness of the resistant, double layered protective coating. A convenient and striking comparative method is to compute the weight loss between untreated nickel base alloy components or bases with the weight loss of the same or equivalent base material as the result of subjection to operative conditions under simulated operative conditions. Here untreated and treated vanes or buckets are placed upon the same or an equivalent gas turbine and the latter run for 120 hours at 1600° F. The components are subjected to the corrosive conditions arising from sulfate attack by the injection into the air intake of the turbine of synthetic sea water, such comprising a solution of sodium sulfate and sodium chloride, as indicated in the foregoing, in the proportions of four parts of such synthetic seat water per million parts of intake air.

The following table sets forth the loss, by way of comparison of untreated base nickel alloys with the treated alloy of this invention:

TABLE II.—COMPARISON OF WEIGHT LOSS DURING SULFIDATION (120 HR. AT 1,600° F.)

Alloy	Coating	Weight loss (percent)
A	None	13.3
A	Al	4.3
A	Cr-Al-Si	0.06
B	None	27.3
D	do	34.0
E	do	32.8

The effectiveness of the nickel alloy two layer treatment, insofar as resistance to sulfidation is concerned, is dramatically demonstrated in the above table. For example, the turbine blades were here made of four different nickel base alloys, all of them, however, falling within the typical formulae of Table I. The letters of each correspond to the similarly lettered alloys of Table I. Alloy A exhibited a substantial weight loss (13.3%) in its uncoated condition. When alloy A was coated with aluminum the weight loss was substantially reduced, to 4.3%. However, when that same alloy, in the form of a turbine blade, was coated or treated by the method of this invention, i.e., with a chromium intermediate layer and aluminum-silicon superimposed thereover, the weight loss was only 0.06%. The much higher weight losses of alloys B, D and E, in the amounts of 27.3%, 34.0% and 32.8%, are even more significant and reflect their lower chromium content.

Since these turbine blades or buckets were subjected to simulated but effective operating conditions involving a sea water atmosphere, it is plain that the treatment of

the invention reduced to a most insignificant degree (0.06% weight loss) the effects of oxidation and sulfidation. It would appear also that the much lower weight loss (4.3%) of the aluminum treatment of alloy A is attributable primarily to a delay in the onset of the corrosive attack.

FIGURE 4 is illustrative of the percentage-wise presence of each of the primary elements (nickel, aluminum, chromium and silicon) in one type of nickel base alloy part or component, identifying the percentage amounts of these elements, in each case, in the substrate, in the diffused zone and in the final, aluminum-silicon layer.

For example, by reference to this figure, it is seen that the matrix or substrate contains 70% nickel, about 4.5% aluminum, 12.5% chromium and about .1% silicon. The significance of the graphs of FIGURE 4 is found particularly in the increase in chromium in the diffused zone to about 17% with a corresponding but lesser increase in aluminum and silicon content in that zone. The nickel in the diffused zone decreases to about 55%. In other words, this diffused zone represents the chromium rich layer.

FIGURE 4 thus illustrates achievement of the underlying aim of the invention—to provide a significant chromium rich layer in the diffused zone which is effective in preventing penetration of sulfur, or formation of sulfides, into the matrix or base alloy.

Such figure is also illustrative of the relatively high aluminum-silicon content of the outer or so-called "build up" layer. Here it is seen that the amount of aluminum is twice that in the substrate; similarly the silicon graph indicates an increase of up to about 2%.

It will thus be appreciated that the base material or nickel alloy matrix was provided with two corrosive resistant overlays—an intermediate diffused zone, which being rich in chromium prevents sulphur penetration or sulfide build up in the matrix, and an outer aluminum-silicon enriched diffused layer which is extremely resistant to the usually corrosive results of oxidation.

Although the present invention has been described in conjunction with the preferred embodiments thereof, it is to be understood that modifications and variations thereof may be resorted to without departing from the spirit and scope of the invention, the latter not to be limited except by the limitations asserted in the following appended claims.

We claim:

1. In a coating process for a nickel base alloy material having a chromium content of less than 16%, plating said material with chromium, dip coating said material with an aluminum-silicon alloy, then post dipping the parts into the molten flux bath maintained at about 1400° F. for up to 30 seconds to attain salt bath temperature and establish the initial diffused alloy layer, removing the excess of aluminum-silicon alloy by replacement thereof with nickel and reacting said nickel with nitric acid, and diffusing said chromium and said aluminum-silicon alloy by heating to a temperature of from about 1975° F. to about 2050° F. for a period of about two hours.

2. The invention as defined in claim 1 wherein said chromium content of the base alloy does not exceed about 10% and said aluminum-silicon alloy is 88% aluminum and 12% silicon.

3. The invention as defined in claim 1 wherein said diffusing step is followed by aging procedures at temperatures lower than 1975° F.

4. A method for treating a nickel base alloy having less than 16% chromium to render said alloy oxidation and sulfidation resistant comprising electro plating said material with chromium to obtain a coating thickness of from about 0.0001 to 0.0005 inch, dip coating said alloy with an aluminum-silicon alloy containing about 88% aluminum and about 12% silicon, then post dipping the parts into the molten flux bath maintained at about 1400° F. for up to 30 seconds to attain salt bath temperature and establish the initial diffused alloy layer, removing the excess of said aluminum-silicon alloy, diffusing chromium and said aluminum-silicon alloy by heating for about two hours at an elevated temperature of about 1975° F. but lower than 2150° F., and aging said base alloy by heat treatments at temperatures lower than said elevated temperature.

5. The method of claim 4 wherein said base alloy contains from 8% to 13% chromium.

6. The method of claim 4 wherein said base alloy contains about 10% chromium.

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U.S. Cl. X.R.

29—197, 498; 117—71; 204—38, 41

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,493,476 Dated February 3, 1970

Inventor(s) Joseph G. Lucas, William R. Freeman, Jr., and Warren A. Rentz

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 31, "or" should read --- of ---.(1st occurrence)
1, line 38, "corosive" should read --- corrosive ---.
1, line 44, "varous" should read --- various ---.
2, line 30, "prolusion" should read --- propulsion ---.
2, line 48, "aloy" should read --- alloy ---.
2, line 59, "vntion" should read --- vention ---.
3, line 51, "wiht" should read --- with ---.
4, Table 1, under Co (Alloy B) "15 0" should read --- 15.0 ---.
4, line 37, "conductive" should read --- conducive ---.
6, line 51, "like" should read --- life ---.
6, line 74, "sulfica-" should read --- sulfida- ---.
7, line 20, "0.001" should read --- 0.0001 ---.
7, line 28, "plate" should read --- plated ---
7, line 65, "washer" should read --- washed ---.
8, line 41, "seat" should read --- sea ---.

SIGNED AND
SEALED
JUL 21 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents