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METHOD OF COATING IRON, NICKEL OR COBALT ALLOY WITH ALUMINUM

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Fig. 2

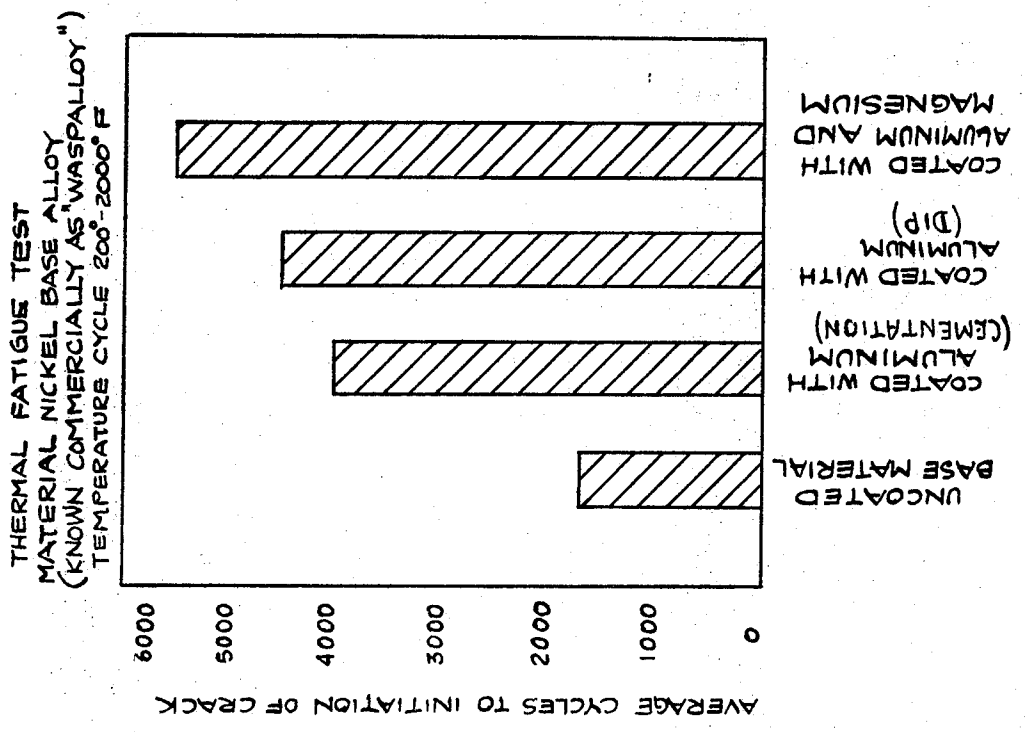
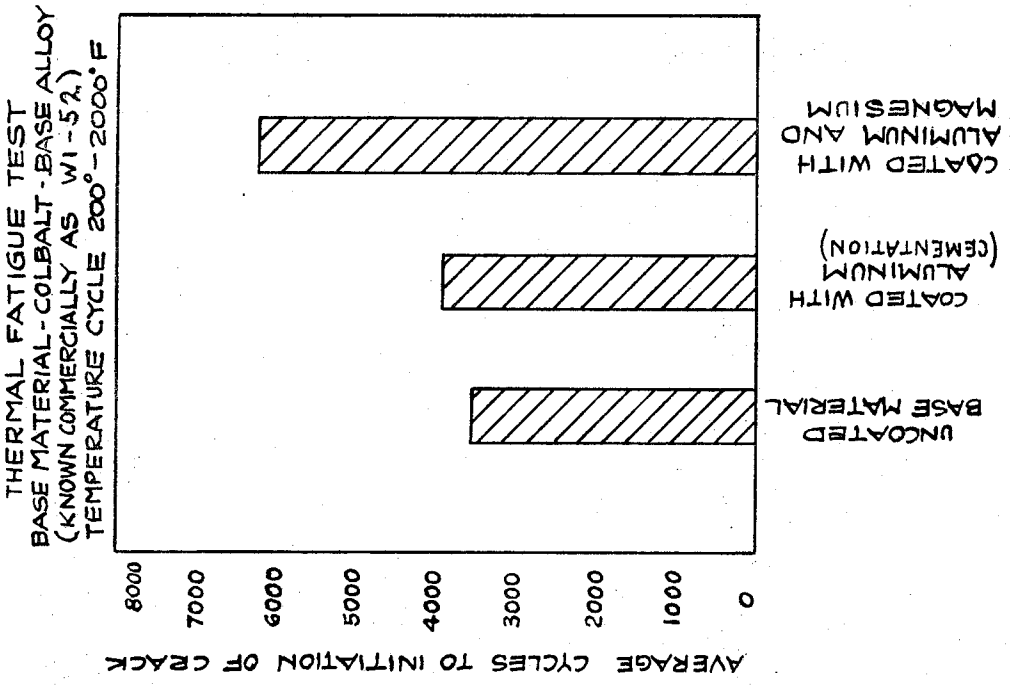


Fig. 1



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METHOD OF COATING IRON, NICKEL OR COBALT ALLOY WITH ALUMINUM

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ABSTRACT OF THE DISCLOSURE

A process for coating an iron, nickel or cobalt base alloy is provided which comprises treating a surface of the selected alloy with a material consisting essentially of from about 10 to 30 weight percent magnesium with the balance being aluminum and then heating the so-treated alloy in a non-oxidizing atmosphere to a temperature above about 1800° F. to cause the aluminum-magnesium material to coat and diffuse into the treated surface of the iron, nickel or cobalt base alloy.

This application is a continuation of application Ser. No. 413,771, filed Nov. 25, 1964, now abandoned.

The present invention relates to coating of metals such as iron, nickel and cobalt base alloys commonly used for gas turbine blading, combustion liners and fuel-air nozzles among other parts. Oxidation and high temperature corrosion and erosion resistance above that possessed by the basic alloys is, of course, the main reason why coatings are necessarily widely used.

One of the best known and useful coatings is produced by diffusing aluminum into the surface of engine parts to a depth of several thousandths of an inch, thereby creating a new alloy with the metals comprising the basic alloy of which the engine part is made.

Such a coating may be made in a variety of ways, such as hot dip, thermal decomposition, electrophoretic deposition and chemical displacement to mention the best known. In some cases, chromium, silicon, cobalt, nickel and iron have been used with the aluminum in an effort to improve the basic characteristics of the new alloy being created in or on the surface of the parts being treated.

In the past such engine parts have comprised nickel, cobalt or iron alloys, and the table which follows gives as an example the composition of typical alloys in this category.

	Nickel alloy (Waspalloy)	Cobalt alloy	Iron alloy
C	0.10	.4-.5	
Mn	0.15	.5	
S	0.015	.04	
Si	0.20	[1].5	
Cr	14.-16.	20-22.	21.0
Co	17.-20.	Bal.	20.0
Mo	4.5-5.5		3.0
Ti	2.75-3.75		
Al	3.75-4.75		
B	.025-.035		
Fe	[1]4.0	[1].6	Bal.
Cu	0.10		
Zr	0.06		
Ni	46.0-54.0	[1]1.0	20.0
W		10.0-12.0	2.5
Cb, Ta		1.5-2.0	.75-1.25

[1] Maximum.

While such prior coatings have served well and represented a considerable improvement over uncoated metal parts, there are definite limitations with respect to the erosion resistance and also the upper temperature limit at which the parts may be safely operated. This is true even with close control of the coating process and under optimum conditions; the products thus coated have bounds which, as the technology of engines advances, are considered to be less and less satisfactory.

In particular, there is a need for the best erosion protection and resistance to thermal fatigue that can possibly be developed in alloy metals.

Accordingly, an object of the present invention is to provide an improved coating and an improved coated product, as well as an improved method for treating or coating heat-resistant metals and alloys, particularly the alloys set forth above and additionally a pack cementation powder mixture associated therewith, by which the upper limits of thermal fatigue are markedly increased without significant detriment to erosion resistance.

Another object of the invention is to provide an improved coated or diffused product, process and treating or coating agent as above set forth, which may be economically carried out or produced both from the standpoint of cost of materials and processing time, as well as from the standpoint of equipment needed.

A feature of the invention resides in the provision of an improved coating method and coating agent which are not especially critical but instead exhibit complete utility under conditions which are considered commercially acceptable for production purposes.

In the drawings:

FIG. 1 is a bar graph involving thermal fatigue, comparing specimens treated in accordance with the invention, with prior art specimens, the base material being a cobalt-base alloy.

FIG. 2 is a bar graph involving thermal fatigue, comparing nickel-base alloy specimens treated in accordance with the invention, with prior art specimens.

We have found that, contrary to what might be expected, the incorporation of very small amounts of the metal magnesium in an aluminum or aluminum alloy coating or diffusion, wherein the various metals involved are alloyed at and with the surface portions of the base alloy structure, provides a surprisingly improved product with respect to thermal fatigue without appreciable detriment to erosion resistance.

Of itself, magnesium is known to be a highly inflammable, unstable metal which reacts violently when its temperature is raised, being unable to withstand elevated temperatures in the manner of most other metals of the temperature-resistant class. Such undesirable properties of magnesium would lead one to believe that its addition or incorporation in an alloy coating for the purpose of increasing the resistance to thermal fatigue would have anything but a beneficial effect.

By actual tests, however, we have found that coatings and diffusions of aluminum or aluminum alloy wherein aluminum is the dominant material, which have very small percentages of magnesium incorporated, change greatly for the better the characteristics of the treated part, by which high temperatures and thermal fatigue are resisted. The improvement effected has been determined from a number of actual, repeated tests made on sample alloy pieces which include iron, nickel or cobalt bases.

We have determined that in certain samples wherein the coating or surface diffusion alloy which contains aluminum also includes approximately from 2% to 6% of magnesium at surface portions of the specimen, there is an increase of resistance to fatigue of roughly from 30% to 50%, without significant detriment to erosion resistance.

The coating or diffusion alloy may with benefit include small amounts of the refractory metal group, including columbium, tantalum, molybdenum and tungsten, as well as small amounts of titanium and chromium. Such coatings and diffusions were employed on alloy parts having metals of the iron group, namely iron, nickel and cobalt.

The results are borne out by the bar graphs of FIGS. 1 and 2. The specimens comprised the iron base, as well as cobalt base and nickel base alloys. The test pieces were subjected to a temperature cycle of 200°–2000° F. During the cycle the pieces were heated to 2000° F. for forty seconds, then blasted with air for twenty seconds followed by non-agitated air cooling for an additional twenty seconds.

Specimens were also subjected to erosion tests, involving exposures for 100 hours at 2000° F. in an oxidizing atmosphere. The specimens passed such tests with weight losses of not more than 0.08 gram which is well within the allowable limit set by turbine engine manufacturers. The initial weight of the specimens in each instance was in the neighborhood of 50 grams.

The treatment or coating and diffusion of the base alloy structure may be done by means of a pack cementation powder mixture or else it may be done by dipping the base alloy structure in a molten bath containing an alloy of aluminum and magnesium and thereafter heat treating the alloy structure after removal from the bath.

The following examples are given of pack cementation powder mixtures which have been utilized in the first-mentioned method and which have produced coated articles of superior characteristic as already indicated.

EXAMPLE 1

Cementation mix of 98.5% of commercial grade aluminum oxide particles having a size of 220 mesh, 1.5% of aluminum-magnesium alloy (10% magnesium) powder having a size to pass through a 20 mesh screen, to which is added 35 grams/100 pounds of hydrazine dihydrochloride as an active gas-producing ingredient. This is packed about the parts to be treated and is heated to 1910° F. ±10% for two hours and allowed to cool. The parts are removed, washed and found to have approximately two mils of alloy coating all over.

EXAMPLE 2

Cementation mix of approximately 98% of aluminum oxide particles having a size of 220 mesh, 1.5% of aluminum powder of size 325 mesh, and .15% of magnesium powder of size 325 mesh, to which is added 35 grams/100 pounds of hydrazine dihydrochloride. The procedure for packing the treating is as given in Example 1.

EXAMPLE 3

Cementation mix: 98.5% of pure Al_2O_3 particles having a size of 220 mesh, 1.5% of aluminum-magnesium alloy (10% mg.) particles having a size of 90 mesh, to which is added hydrazine dihydrochloride in the proportion of 35 grams/100 pounds. The procedure followed is as given in Example 1.

EXAMPLE 4

A cementation mix consisting of 97% of commercially pure aluminum oxide particles having a size of 220 mesh, 1½% of aluminum-magnesium alloy particles (30% magnesium) having a size of 325 mesh, 1½% of aluminum powder having a size of 325 mesh, to which is added 35 grams/100 pounds of hydrazine dihydrochloride as an active gas-producing ingredient. Subsequent procedures are as above.

An example of a method involving dipping the pieces in a molten bath is as follows:

EXAMPLE 5

A bath of aluminum-magnesium alloy, containing 10% to 30% magnesium held at 1320° F. to 1375° F. is used to coat an engine blade or vane, as by dipping a prepared piece in the bath. After coating, the excess molten metal is removed by brushing, vibrating or otherwise. The initial coating is then diffused to form the final alloy coating by heating the piece in a neutral or reducing atmosphere for approximately four hours at 1975° F. to give a final alloy thickness of .003 all over. Diffusion will vary with the base alloy heat treatment and the temperature to which the part is subjected.

A careful analysis of coated cobalt-base alloy structures treated by the above methods has revealed the following make-up of the surface areas and areas immediately under the surface.

SPECIMEN #1

On surface

	Percent
Al	50–55
Co	18–20
Cr	5–7
W	1–2
Ti	0–3
Fe	0.5–1.0
Zn	3–4

Also, some ZnO and Al_2O_3 on surface.

At surface after slight buffing

	Percent
Al	45–50
Co	34–38
Cr	7–9
W	3–4
Ti	3–5
Fe	1–2
Mg	2–3

No zinc.

SPECIMEN #2

On surface

	Percent
Al	45–50
Co	14–16
Cr	1–2
W	4–5
Ti	2–3
Fe	0.2–0.5
Mg	4–6

Also, Al_2O_3 on surface and no Zn present.

At surface after slight buffing

	Percent
Al	28–32
Co	47–51
Cr	12–15
W	5–7
Ti	1–2
Fe	1–2

It will be noted that the surface portions of the specimens are constituted of an alloy comprised of the base alloy, aluminum in quantities of roughly 50% and magnesium in quantities of several percent, being indicated as in the range of from 2% to 6%, these figures being non-critical in that somewhat smaller or larger percentages also provide an improved product but with different characteristics from those indicated in the specified tests.

The above analysis was made with an electron beam microanalyzer using X-rays and a single crystal X-ray spectrometer which provides a spectrum analysis. This equipment has revealed the chemistry of the outer surface of samples coated according to the invention, as well as that of the metallic coating layers just beneath the outer surface, which layer is exposed by subjecting the samples to a slight buffing.

The base structure of the specimens comprised a cobalt base alloy known commercially as W1–52 and having approximately 20% to 22% chromium, 10% to 12% tungsten, .6% iron and the balance cobalt.

The presence of cobalt and nickel and iron is explained because these are derived from the cobalt base, nickel base or iron base alloys themselves. Titanium and chromium occur, as well as metals of the refractory group,

which group includes niobium, columbium, tantalum, molybdenum and tungsten, and it is at present believed that some metals of the above list are due to impurities in the aluminum and mixes used in the specific coating procedure that was analyzed, and that they contribute beneficially to the improved end result.

In addition to the cementation and dip procedures, a slurry may be utilized. Such a slurry involves particles in suspension and a binder, by which the parts are coated prior to heat treatment. The slurry may comprise an alloy powder of aluminum magnesium constituted, for example, of 90% aluminum and 10% magnesium. From 25 to 75 parts by weight of this powder may be used with 75 to 25 parts of flux, such as a fluxing substance known commercially as "Cryolite." Cryolite may be made up of 40% of KCl, 40% NaCl, 6% lithium fluoride and the balance comprising sodium fluoride and aluminum fluoride in the form of $3NaF—AlF_3$. From 40% to 80% of a liquid vehicle and 2% of a binder may be used with the novel pack composition provided by the invention. and thereafter heat-treated at temperatures sufficiently high to diffuse and alloy the aluminum and magnesium into the parts.

As at present understood, the improved results obtained in the specimens by practicing the invention are the consequence of alloying small amounts of magnesium with aluminum or aluminum alloys and with the base alloy of the specimens, whether such base alloy is of the cobalt type, or nickel or iron type. The specific examples given above of the cementation packs are merely illustrative of the novel pack composition provided by the invention. The method of the invention, embracing the alloying with magnesium by either a cementation pack, molten bath or a slurry, has also been explained, as well as the improved product comprising the coated and diffused pieces and the chemical make-up thereof involving the alloying of magnesium and aluminum, or aluminum alloy.

As already noted, the invention is of particular importance in the producing of parts such as vanes or blades, nozzles, combustion liners and the like for use with gas turbines where oxidation, high temperature fatigue and erosion represent major factors in the operation. The invention has utility in the production of coated and diffused or alloyed parts for all types of high temperature applications, as will be understood.

In accordance with the invention, a machine part such as a piece formed of Waspalloy (nickel) alloy may be advantageously first coated or diffused with chromium, and thereafter have the magnesium-containing coating applied. A cementation pack may be initially used, which includes powdered ferro-chromium alloy (65% Cr and 35% Fe) in a quantity of approximately 65% by weight, about 1½% of ammonium fluoride NH_4F and alumina powder such as the oxide Al_2O_3 to make up the balance (approximately 33½% by weight). With the pack at about 1850° F. for five or six hours a chromium deposit in the neighborhood of .001" to .002" will be effected. Thereafter the processing to effect the coating containing magnesium may be done, as explained above.

If the presence of iron is considered deleterious in the treated piece due to specialized requirements, the cementation pack may utilize chromium in another form which is devoid of iron, as will be understood.

An iron-containing cementation powder mixture which may be advantageously utilized, in accordance with the invention, comprises approximately 40% ferro-aluminum, approximately 40% aluminum oxide, not more than 20% magnesium oxide and traces of a gas-producing agent such as hydrazine dihydrochloride. Such mixture effects a diffusion containing magnesium, as with the other examples given above.

In the light of the present invention and disclosure, variations and modifications to meet the individual whim or particular need will doubtless become evident to those skilled in the art, to obtain all or part of the benefits outlined above without copying exactly the specific examples given herein, and we therefore claim all such insofar as they fall within the reasonable spirit and scope of the appended claims.

What is claimed is:

1. The method of coating a metal alloy structure having an iron or nickel or cobalt base, which comprises treating the structure with exclusion of air at a temperature of more than 1800° F. with a source of both aluminum and magnesium wherein the magnesium is present in quantities ranging from about 10 to 30 weight percent with the balance essentially aluminum.

2. The method of coating a metal alloy structure having an iron or nickel or cobalt base, which comprises treating the structure with the exclusion of air at a temperature of approximately 1800° F. to 2000° F. with a material consisting essentially of a small amount of finely divided particles of aluminum and magnesium, and an inert material and traces of a source of gaseous halogen, wherein said finely divided particles are present in the amount of between 10% and 30% by weight magnesium and the balance essentially aluminum.

3. The method of coating a metal alloy structure having an iron or nickel or cobalt base, which comprises treating the structure with exclusion of air at a temperature of approximately 1800° F. to 2000° F. with a mixture of finely divided particles comprising aluminum oxide and aluminum magnesium alloy, and traces of a source of gaseous halogen, wherein the weight percent of magnesium based on the entire mitxure is from about .15 to 1% and said weight percent aluminum oxide is at least 97% based on the entire mixture.

4. The method of coating a metal alloy structure having an iron or nickel or cobalt base, which comprises treating the structure with exclusion of air at a temperature of approximately 1800° F. to 2000° F. with a mixture of finely divided particles comprising aluminum oxide, aluminum powder and magnesium powder and traces of a source of gaseous halogen, wherein the weight percent of magnesium based on the entire mixture is from about .15 to 1% and the weight percent of aluminum oxide is at least 97% based on the entire mixture, the balance being aluminum powder.

5. In a process of applying an aluminum magnesium coating to a metal alloy structure having an iron or nickel or cobalt base by the steps of surrounding said structure with the donor material, which material includes a small amount of active constituents consisting of magnesium in a weight percent of from about 10 to 30 with the balance being essentially aluminum, traces of a source of gaseous halogen and an inert material; and heat treating the said structure in an atmosphere free from oxygen to a temperature of at least 1800° F.; the combination in which the active constituents of the donor material comprise an alloy of aluminum and magnesium.

6. In a process of applying an aluminum magnesium coating to a metal alloy structure having an iron or nickel or cobalt base by the steps of surrounding said structure with the donor material, which material includes a small amount of active constituents consisting of magnesium in a weight percent of from about 10 to 30 with the balance herein essentially aluminum traces of a source of gaseous halogen and an inert material; and heat treating the said structure in an atmosphere free from oxygen to a temperature of at least about 1800° F.; the combination in which the active constituents of the donor material comprise a powder of aluminum and magnesium.

7. In a process of applying an aluminum magnesium coating to a metal alloy structure having an iron or nickel or cobalt base by the steps of surrounding said structure with the donor material, which material includes essentially magnesium in a weight percent of from about 10 to 30 with the balance being essentially aluminum, the combination in which the donor material comprises a

molten alloy bath of aluminum and magnesium held at a temperature in the neighborhood of 1300° F.; and heat treating the said structure in an atmosphere free from oxygen to a temperature of at least 1800° F.

8. The combination of claim **5**, wherein the inert material is aluminum oxide.

9. The method of coating an iron, nickel or cobalt base alloy structure, which comprises depositing chromium on a surface of said alloy and then treating the structure with exclusion of air at a temperature of approximately 1800° F. to 2000° F. with a mixture of powders containing as ingredients an inert material, a source of halogen gas and a small quantity of the metals aluminum and magnesium, wherein the aluminum and magnesium metal constituents consist essentially of 10% to 30% by weight magnesium and the balance aluminum.

10. The method of coating a metal alloy structure having an iron or nickel or cobalt base which comprises treating the structure with the exclusion of air with a material consisting essentially of particles of aluminum and magnesium, an inert material and traces of a source of gaseous halogen, at a temperature sufficiently high to diffuse and alloy aluminum and magnesium into the structure, said particles being originally present in an amount between 10% and 30% by weight magnesium and the balance essentially aluminum.

11. The method of coating a metal alloy structure having an iron or nickel or cobalt base which comprises treating the structure with exclusion of air with a mixture of finely divided particles comprising aluminum oxide and aluminum magnesium alloy, and traces of a source of gaseous halogen, wherein the weight percent of magnesium based on the entire mixture is from about 0.15% to 1% and said weight percent of aluminum oxide is at least 97% based on the entire mixture, and treating said structure with said mixture at a temperature sufficiently high to cause diffusion of aluminum and magnesium into the structure.

12. The method of coating a metal alloy structure having an iron or nickel or cobalt base which comprises treating the structure with the exclusion of air with a mixture of finely divided particles comprising aluminum oxide, aluminum powder and magnesium powder, and traces of a source of gaseous halogen, wherein the weight percent of magnesium based on the entire mixture is from about 0.15% to 1% and the weight percent of aluminum oxide is at least 97% based on the entire mixture, the balance being the aluminum powder, and treating said structure with said mixture at a temperature high enough to cause diffusion and alloying of aluminum and magnesium into the structure.

References Cited

UNITED STATES PATENTS

1,706,130	3/1929	Ruder.	
2,300,400	11/1942	Axline.	
2,406,245	8/1946	Oganowski et al.	
2,664,874	1/1954	Graham.	
2,752,265	6/1956	Whitfield et al.	
2,774,686	12/1956	Hodge	117—114
3,026,606	3/1962	Nickola	117—114X
3,055,711	9/1962	Sprowl	117—114

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