

[72] Inventor **David J. Levine**
Cincinnati, Ohio
[21] Appl. No. **780,177**
[22] Filed **Nov. 29, 1968**
[45] Patented **Nov. 2, 1971**
[73] Assignee **General Electric Company**

[54] **HIGH TEMPERATURE METALLIC DIFFUSION
COATING AND METHOD**
4 Claims, No Drawings
[52] U.S. Cl. **117/107.2 P,**
117/107.2 R
[51] Int. Cl. **C23c 9/02**
[50] Field of Search **117/107.2**
P, 107.2, 46 CA

[56] **References Cited**
UNITED STATES PATENTS
3,415,672 12/1968 Levinstein et al. 117/107.2 X
3,477,831 11/1969 Talboom et al. 117/46 X
Primary Examiner—Alfred L. Leavitt
Assistant Examiner—Wm. E. Ball
Attorneys—Derek P. Lawrence, E. S. Lee, III, Lee H. Sachs,
Frank L. Neuhauser and Oscar B. Waddell

ABSTRACT: Improved oxidation and sulfidation resistance can be imparted to a high-temperature metallic diffusion coating diffusion bonded with metallic surface, such as a nickel, cobalt or iron base alloy surface, by embedding in a coating outer portion between about 5 and 50 volume percent of oxide particles of up to about 20 microns in size and thermally stable to at least about 2000° F.

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One manner for increasing the operating life of a high temperature operating component in modern power producing apparatus such as turbine engines is to interdiffuse with the component's surface a protective high temperature coating. A number of these types of coatings have been reported and are well known in the coating art as high temperature diffusion type coatings.

A specific type of coating to which the present invention relates is described by copending application Ser. No. 693,691 filed Dec. 14, 1967, now Pat. No. 3,540,878, and assigned to the assignee of the present invention. Described in that copending application is a ternary alloy useful in a multicomponent particulate mixture and in a metallic diffusion type coating method. The alloy consists essentially of, by weight, about 50-70 percent Ti, 20-48 percent Al and 0.5-9 percent combined carbon and has a dispersion of Ti_2AlC complex carbide in a matrix of Ti or Al or their alloys. The particulate mixture includes, along with the alloy and an inert filler, about 0.1-10 weight percent of a halide salt activator which will react with a metallic element in the ternary alloy to form a halide of such metallic element under sufficient time and temperature conditions in a nonoxidizing atmosphere. Preferred are chlorides and fluorides of ammonium and of the alkali metals of Group I A of the Periodic Table of Elements. Specifically preferred is about 0.1-2 percent of halides selected from NaF, KF, NH_4Cl and NH_4F .

The diffusion type coating of unusual characteristics which results from use of that described method is presently being applied in production use. However, despite the benefits of the coating defined by the above identified copending application and other similar coatings, it has been recognized that still further improvement is desired, not only to resist oxidation but also to resist sulfidation, sometimes referred to as hot corrosion.

It is a principal object of the present invention to improve the coating of the type which results from practice of the invention of the above identified copending application by providing a coating of an improved combination of oxidation and sulfidation resistance.

Another object is to provide such an improved coating having an outer portion which will act as an interdiffusion barrier between oxidizing and sulfidizing environments around a coated article and the article basis metal.

These and other objects as well as the advantages of the present invention will be more fully understood from the following detailed description and examples which are typical of the present invention defined by the appended claims.

It has been recognized that an improved combination of oxidation and sulfidation resistance can be obtained in a diffusion bonded coating of about 1-5 mils as measured in the as-coated condition by embedding in an outer portion of the coating, such as the one described in the above identified copending application, about 5-50 volume percent of entrapped oxide particles of about 1-20 microns in size and thermally stable to at least about 2000° F. Such dispersion in the outer portion can be accomplished, according to the method form of the present invention, by first applying to a surface of an article to be coated an interim coating of about 1-25 mils in thickness of such oxide particles in a nonfused, loosely held, vapor permeable condition and of a type which will not enter into the reaction of the metallic diffusion coating. Then the metallic diffusion coating, such as defined by the above-identified copending application, penetrates through the particles of the interim coating entrapping the particles in the coating outer portion during the heating cycle. Because the oxide particles are about 1-20 microns in size and thus are larger than a size which would allow them to move interstitially into the basis metal or alloy, the oxide particles are confined to the coating outer portion.

The useful life of metallic diffusion coatings applied to high temperature operating components such as of a gas turbine engine is dependent in a significant amount on the stability of the interface between the coating and the basis metal to which it has been applied. Of course, such coating life is further dependent upon coating surface degradation resulting from contact with erosive, corrosive or oxidizing environments. However, inhibition of diffusion through the coating of oxidizing and sulfidizing agents toward the coating basis metal interface can significantly lengthen the useful life of the coating. The present invention recognizes that the introduction of the above defined oxide particles in an outer portion of the coating results in such a barrier to that undesirable migration.

As a specific example, one form of the above described ternary alloy powder used in the evaluation of the present invention consisted nominally, by weight, of 61 percent Ti, 34 percent Al, and about 4.5 percent combined carbon. This ternary alloy in powder form will be hereinafter identified as "Alloy C." Prior to the preparation of specimens for the evaluation of the present invention, a blend of about 40 weight percent Alloy C powder and about 60 weight percent Al_2O_3 powder was mixed with about 0.2 weight percent NH_4F . In this type of particulate mixture, the Al_2O_3 powder acts to inhibit sintering of the Alloy C powders but does not enter into the coating process.

The method of the present invention contemplates the application to the surface of an article to be diffusion coated of oxide particles, stable both to the processing temperature and mechanism, as an interim or preliminary coating in a nonfused, loosely held vapor permeable condition. This can be and was in this example accomplished by first making a slurry of the oxide particles and a liquid binder which will decompose without residue upon heating. For example, an acrylic resin in toluene or acetone can be used. As will be discussed later, the thickness of the interim coating is not critical. Therefore, the slurry can be adjusted in concentration to provide, for example, from about 1-25 mils of oxide on the surface. However, from a practical viewpoint no more than about 15 mils is necessary. Although the oxide particles are no more than about 20 microns in size, it is preferred that a variety in size of particles be present rather than particles all of the same size.

A variety of oxides of thermal and process stability, including oxides of titanium, aluminum and their mixtures, have been evaluated in connection with the present invention. It is preferred that TiO_2 or Al_2O_3 or their mixtures in particle sizes of about 1-20 microns be used in the present invention when coating surfaces based on one of the elements Fe, Ni or Co.

The slurry can be applied to the article surface by a variety of methods such as brushing, dipping, spraying, etc. In this example, a paint spray gun was used with a slurry to apply a coating of a powder mixture of about 50 weight percent each of Al_2O_3 and TiO_2 .

After application of the oxide coating to the article surface to be coated, the article was placed in a container, such as retort, along with the previously described particulate mixture, including powdered Alloy C. It should be recognized, however, that as indicated before, the Al_2O_3 in the particulate mix is included as a filler and does not enter into the coating reaction. Therefore, if a method such as is described in copending application Ser. No. 780,199, filed concurrently with this application, in which the article surface to be coated does not physically contact the coating material such as the particulate mixture, then the filler may be eliminated if particle sintering is not a problem. If the article is to be contacted by the particulate mixture as described in the above identified copending application Ser. No. 693,691, then inclusion of the Al_2O_3 filler is preferred.

The retort enclosing the particulate mixture and the article surface including the interim oxide coating was provided with a nonoxidizing atmosphere, in this example hydrogen, and was heated in the range of 1400-2100° F. for 1-4 hours, for example, about 1950° F. for 3-4 hours. This time and temperature was sufficient to allow deposition of such elements as alu-

minum and titanium from powdered ternary Alloy C, through their halide vapor state, onto the article surface by first penetrating through and subsequently entrapping the particles of the oxide of the interim coating. The time and temperature selected must be sufficient to allow further interdiffusion between the deposited elements and the article surface.

After cooling, the treated article surface was removed from the retort. Loosely adhering excess powders either from the particulate mix, if the article contacted such mix, or from the interim oxide coating, or both, were removed from the coated surface. It has been found that although relatively thick interim coatings of oxides can be applied to the surface, the titanium or aluminum or both from the ternary alloy powder will penetrate through the excess oxides to leave them only loosely adherent and readily removable from the surface after processing. Thus a reasonable excess thickness of the interim coating is not critical. It is preferred that about 2-10 mils of oxide be applied as the loosely adherent, nonfused, vapor permeable particles comprising the interim coating.

Practice of the method of the present invention provides an article surface, particularly one based on Fe, Ni or Co, with a diffusion bonded, two portion coating: a coating outer portion and a coating inner interdiffusion portion. Each portion includes primarily intermetallics formed from the basis element, for example, Ni, Co or Fe, and certain of any alloying elements of the article surface, with metallic diffusion coating elements such as titanium, aluminum, etc. The intermetallics result from interdiffusion between elements of the coating and of the basis metal or alloy. As was stated before, the entrapped oxide particles in the coating outer portion, because of their size in the range of about 1-20 microns, cannot move interstitially with respect to the basis metal in the formation of coating inner diffusion portion between the outer portion of the coating and the article surface. Therefore only the coating outer portion includes, in addition to the intermetallics, entrapped oxide particles.

It has been found in the evaluation of the present invention that the coating inner interdiffusion portion and the coating outer portion together in the as-coated condition must represent a thickness no greater than about 5 mils. Thicknesses in excess of that amount result in coatings having poor adherence properties.

It has been recognized further that amounts of oxide particles less than about 5 volume percent provide no benefit over a coating without such oxide particles. Amounts of entrapped oxide in excess of about 50 volume percent results in significantly reduced coating erosion resistance. Therefore, the present invention contemplates a coating the outer portion of which includes, in addition to the above described intermetallics and diffusion products, about 5-50 volume percent of dispersed oxides.

The oxides preferred for dispersion in the outer portion of the coating in the practice of the method of the present invention in coating Fe, Ni or Co base alloys, include Al_2O_3 or TiO_2 or their mixtures. If such a mixture of oxides is used, it has been found that about 50 percent by weight of each is a satisfactory mixture and that a varied size mixture of particles is preferred in the range of 1-10 microns.

As shown in the above identified copending application Ser. No. 693,691, the type of diffusion coating with which this invention is particularly concerned can be applied to alloy surfaces based on elements selected from Ni, Co and Fe. Typical of data generated in the evaluation of the present invention is that relating to high temperature nickel base superalloys, the compositions for which are shown in the following Table I as including such alloying elements as Cr, Co, Mo, W, Al, Ti, Fe, etc.

TABLE I

Composition Wt. percent—Bal. Ni and incidental impurities

Alloy	C	Cr	B	Co	Mo	Ti	Al	Zr	V	Cb/		
										Ta	W	Fe
1.....	*.1	19	.01	11	10	3.2	1.5					
2.....	.17	9.5	.01	15	3	4.2	5.5	.06	.1			
3.....	.14	13	.01		4.5	0.8	6	.1		2.3		
4.....	*.15	17.5		17	4.0	3	3					
5.....	.1	22		1.5	9						0.6	18.5

*Maximum.

Specimens of each of the nickel base alloys listed in Table I were coated in the manner described in the above specific example: A mixture of 50 percent by volume each of Al_2O_3 and of TiO_2 of particle size in the range of 1-10 microns was applied as an interim coating by spraying from a slurry of the oxide particles and acrylic resin in acetone. The coating method was conducted at about 1950° F. for 3-4 hours in a hydrogen atmosphere. The resulting coating had a coating outer portion, including the entrapped oxides, of about 1 mil thick and a coating inner interdiffusion portion of about 1 mil thick for a total coating thickness of about 2 mils. The oxide particles in the coating outer portion comprised about 10-20 volume percent of the outer portion.

After coating, these specimens along with specimens coated without the interim oxide coating were tested under static oxidation conditions at 2100° F. for 100 hours. Typical of the results obtained are those shown in the following table II.

TABLE II

STATIC OXIDATION: 2100° F.—100 hrs.

% Coating Consumed

Alloy	Metal alone	Metal + oxide
1	75	less than 1
5	50	less than 1

As shown from the data of table II, both coatings protected base metal adequately for 100 hours at 2100° F. However, the life of the coating including the entrapped oxide particles in the coating outer portion is significantly greater as evidenced by less than 1 percent of it being consumed compared with consumption of 50-75 percent for the non-oxide bearing metallic diffusion coating. Therefore, the improved coating of the present invention would continue to protect the article many times longer than the same coating without embedded oxides.

Another series of specimens coated in the same manner were placed in a hot corrosion testing apparatus cycled between about 1650 and 1725° F. Heat was generated from combustion of a natural gas/air mixture. At the same time, 100 parts per million of an aqueous sulfidizing corrodant containing about 9 percent NaCl and about 10 percent Na_2SO_4 was injected toward the specimens. Results of the hot corrosion testing is shown in the following table III.

TABLE III

100 Hr. Cyclic Hot Corrosion Test

Coating Life (hours)

Basis Alloy	Metal alone	Metal + Oxide*
1	25	100 +
2	15	100 +
3	10	100 +
4	45	100 +

*no failure at end of 100 hour test.

As can be seen by the data of table III, in the hot sulfidizing atmosphere described, the life of the coating of the present invention is significantly better than the same coating without entrapped oxides, even though both coatings were capable of withstanding more than 100 hours under oxidizing conditions alone as shown by the data from which table II was selected.

Thus, although the coating described by the above identified copending application Ser. No. 693,691 has significant benefits and uses particularly under oxidizing conditions, it has been recognized that the practice of the present invention provides an unexpected and significant improved combination of hot corrosion or sulfidation resistance along with oxidation resistance.

We claim:

1. In a diffusion method for applying a metallic coating to an article having a metallic surface including a basis metal element selected from the group consisting of Fe, Ni and Co, the steps of:

applying to the surface an interim vapor permeable coating of about 1-25 mils in thickness of loosely adherent, non-fused, oxide particles of about 1-20 microns in size, thermally stable at least to about 2000° F. and which are stable during the diffusion method; and then

applying a metallic diffusion coating of about 1-5 mils in thickness to the surface through the interim coating to entrap oxide particles in a coating outer portion.

2. In the method of claim 1 in which the oxide particles are oxides selected from the group consisting of oxides of Al, Ti and their mixtures; and the metallic diffusion coating is applied by:

placing the article surface in a container including a mixture comprising:

a. a ternary alloy consisting essentially of, by weight, about 50-70 percent Ti, 20-48 percent Al and 0.5-9 percent combined carbon, the alloy having a dispersion of Ti₂AlC complex carbide in a matrix selected from the group consisting of Ti, Al and their alloys, and

b. about 0.1-10 weight percent of the mixture of a halide salt activator which will react with a metallic element in the ternary alloy to form a halide of the metallic element;

providing the container with a nonoxidizing atmosphere;

and then

heating the surface and the mixture in the nonoxidizing atmosphere at a temperature and for a time sufficient (1) to form a halide vapor of at least one metallic component of the ternary alloy, (2) to allow penetration of the vapor through the interim coating to the metallic article surface to deposit the metallic component on the surface and (3) to allow both

i. diffusion of the deposited metallic component with the article surface and

ii. entrapment of particles of the interim coating by the deposited metallic component

to provide the metallic coating comprising a coating outer portion including the entrapped oxides and a coating inner interdiffusion portion intermediate of and diffusion bonded with both the article surface and the coating outer portion.

3. The method of claim 2 in which:

the basis element is Ni;

the interim coating is about 1-15 mils in thickness;

the halide salt activator is selected from the group consisting of chlorides and fluorides of ammonium and of the alkali metals of Group I A of the Periodic Table of Elements; and

the article surface and mixture are heated at a temperature of about 1400-2100°F. for about 1-4 hours.

4. The method of claim 3 in which:

the article surface when enclosed in the container is contacted by the mixture in particulate form; and

the mixture consists essentially of, by weight:

a. about 20-90 percent of the powdered ternary alloy;

b. about 10-80 percent of an inert filler material which will not react with other components of the mixture during use of the mixture; and

c. about 0.1-10 percent of the halide salt activator.

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