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METALLIC SURFACE TREATMENT MATERIAL

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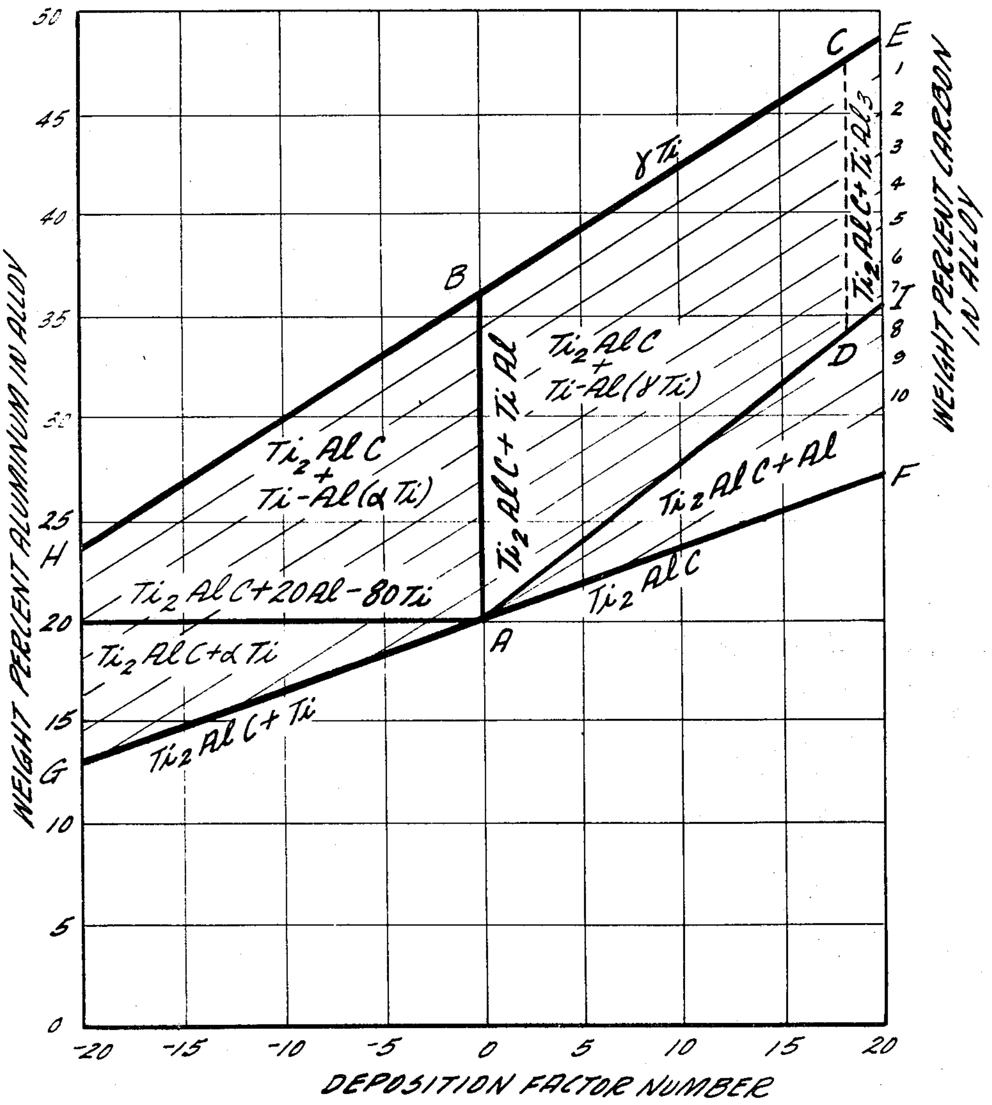

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METALLIC SURFACE TREATMENT MATERIAL

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ABSTRACT OF THE DISCLOSURE

The metallic powder produced from a ternary alloy of Ti, Al and C, having a dispersion of Ti_2AlC complex carbide in a matrix of Ti or Al or their alloys, preferably the binary Ti-Al with the Ti within the gamma range of the Ti-Al phase diagram and avoiding detrimental amounts of $TiAl_3$, allows accurate control of the desposition of either or both Al and Ti or their alloys in a diffusion pack-type method. Deposition is brought about through the use of a halide salt activator preferably in the fluoride or chloride class.

The pack diffusion treatment of metallic surfaces, particularly those based on one or more of the elements iron, nickel and cobalt, has been discussed in the literature and is the subject of copending patent application Ser. No. 410,645, filed Nov. 12, 1964, now U.S. Pat. No. 3,415,672, issued Dec. 19, 1968, assigned to the assignee of the present invention. This type of coating or surface treatment has been effective and is now used in protecting certain superalloy surfaces from oxidation at elevated temperatures. Many of the reported surface treatments and coatings, like that of the present invention, have as their principal intended use the protection of components in modern power producing apparatus, such as turbine components of jet engines, exposed to air and combustion products at temperatures in the range of 1800° F. or above.

As the technology for such power producing apparatus is advanced, pushing the operating temperatures higher and higher, and as the applications for such power producing apparatus have involved more stringent conditions, a need has arisen to protect metallic surfaces not only from oxidation and erosion but also from hot corrosion damage. Resistance to hot corrosive attack is particularly important for the use of jet engines in the vicinity of bodies of salt water.

The application of a coating to jet engine components should change as little as possible the dimensions and weight of the article, principally for aerodynamic reasons and because many such components are required to be made very precisely. Thus eliminated from consideration are many of the variety of coatings or surface treatments available through normal electrodeposition, flame spraying, molten baths and the application of films such as sheet metal cladding. Although some of those methods produce surfaces which can withstand elevated temperature conditions, they produce a change in the dimensions and weight of the article.

A principal object of the present invention is to provide an improved superalloy surface treatment method which, while substantially maintaining the original dimensions and surface finish of an article, provides both oxidation and hot corrosion protection particularly for the article's surface based on one or more of the elements iron, cobalt and nickel.

Another object is to provide an improved alloy and particulate mixture including that alloy, useful in the control of the application of the elements titanium, aluminium or their combinations to such article surfaces.

Still another object is to provide an improved surface treatment method and material for the application of titanium, aluminum or their combinations through the judicious selection of such particulate mixture.

These and other objects and advantages will be more clearly understood from the following detailed description, representative examples and the drawing which is a graphical phase relationship associated with Ti, Al and C.

Briefly, in one form, the present invention provides a particulate mixture of a powdered ternary alloy of Ti, Al and C in the range, by weight, of about 50–70% titanium, 20–48% aluminum and 0.5–9% combined carbon. The alloy has a dispersion of substantially acicular Ti_2AlC complex carbide in a matrix of Ti or Al or their alloys, preferably the binary Ti-Al with the Ti in the gamma range of the Ti-Al phase diagram. The particulate mixture includes a halide salt activator which will react with the metallic elements in the ternary alloy to form a halide. The activator preferably is one selected from the chlorides and fluorides of NH_4 and of the alkali metals in Group I-A of the Periodic Table of Elements. A most practical activator is a halide salt selected from NaF, KF, NH_4Cl and NH_4F, and included in an amount of about 0.1–10 weight percent of the mixture.

One aspect of the present invention is the recognition of a significant relationship between aluminum, titanium and carbon, referred to herein as the Deposition Factor or (D/F). This relationship is a common denominator for control of the method of the present invention through the use of the particulate mixture especially for the codeposition of Al and Ti. It is useful in defining the aluminum concentration in the Ti-Al matrix form of the ternary alloy in relation to the stoichiometric TiAl compound composition, for use in a diffusion type coating process to which the present invention relates.

The above identified copending application, assigned to the assignee of the present invention, describes a binary Ti-Al alloy for use in a diffusion or pack-type coating process to which the present invention also relates. The deposition from such a binary Ti-Al alloy has resulted in very useful coatings under certain conditions. However, it has been found necessary to include hot corrosion resistance as well as oxidation resistance in a coating system for more corrosive conditions at elevated temperatures.

It was recognized that when the elements titanium, aluminum and carbon are included in a ternary alloy in the particular compositions range of 50–70% Ti, 20–48% Al and 0.5–9% C (combined), there is formed a multiphase system which includes a matrix, one form of which is a binary Ti-Al alloy having a dispersion of Ti-AlC complex carbide. It was further recognized that the deposition of either aluminum, titanium or both from such a multiphase system, as required for the particular surface being treated, can be controlled when the ternary alloy is in a powder or particulate form and is mixed with an appropriate type of halide salt activator.

The composition range of the ternary alloy of the present invention is particularly suitable for control of the codeposition of aluminum and titanium or, if desired, individually of aluminum or of titanium. This will be discussed in more detail in connection with the drawing. However, during the evaluation of such a ternary alloy as a powder in a pack diffusion coating process, it was recognized that a difference in coating behavior was at least partially based on the carbon content of the alloy. Powders including combined carbon below about 0.5 weight percent responded differently than those within the range of about 0.5 to about 9 weight percent combined carbon.

It was found that the carbon is needed to form the complex carbide Ti_2AlC. Below about 0.5 weight percent, insufficient carbon is present to fully perform such a function. Also, it was recognized that a unique and very significant interaction between carbon and the elements aluminum and titanium, within the range of about 0.5–9 weight percent combined carbon, allows control of the relative deposition of titanium and of aluminum through the judicious selection of the amount of carbon which can combine in the alloy to form the Ti_2AlC complex carbide. This relationship, called the Deposition Factor, can be reduced to a mathematical form as is described later. Through the use of this relationship, a coating system can be tailored specifically for the superalloy surface to which it is to be applied as well as for the application of the article including such surface. For jet engine parts, this invention is significantly useful to co-deposit and diffuse both aluminum and titanium into superalloy surfaces, particularly those based on the elements nickel or cobalt.

The particulate pack mixture used in the practice of the method of the present invention includes a powder of the multiphase ternary alloy of Ti, Al and C in the above defined range; an inert filler material, which will not react with other components of the mixture, to prevent powder sintering; and a halide salt activator, preferably of the above defined type, which reacts with the elements to be deposited to form a volatile compound. One filler material which has been found to be satisfactory and which was used extensively in the evaluation of the present invention is the refractory oxide Al_2O_3 powder, comprising about 10–80 weight percent of the total pack mixture. During preparation of such mixture, the filler powder, the powdered ternary alloy and the activator are blended together such as in an ordinary powder blender.

The ternary alloy powders described here in connection with the present invention were prepared by vacuum induction melting virgin materials into an ingot of desired composition. The ingot was then pulverized to obtain a powder, for example −100 mesh, which has been found to be suitable for the practice of the method of the present invention.

Typical of examples of the ternary alloy of Ti, Al and C evaluated in connection with the present invention, are those shown in the following Table I. The amount of carbon shown is that analyzed and found to be combined as the Ti_2AlC complex carbide. The Ti_2AlC complex carbide was specifically identified by chemical analysis of the acicular phase residue extracted from the matrix as well as by electron microprobe analysis. X-ray diffraction testing identified the Ti_2AlC complex carbide as having an hexagonal close packed lattice parameter rather than the known cubic structures usually found in the alpha Ti range. Some of the alloy powders included small amounts of uncombined carbon. For instance, the alloy of Example 1 included about 3% uncombined carbon. During evaluation, such uncombined carbon was not recognized to have any detrimental effect on the present invention.

TABLE I.—BALANCE IMPURITIES AND UNCOMBINED CARBON

	Composition weight percent			
Example	Ti	Al	C*	D/F
1	56.4	28.7	9.08	17.2
2	54.7	36.5	4.73	15.7
3	58.9	34.5	5.75	14.3
4	58.6	33.2	6.00	13.7
5	58.4	34.7	5.04	13.6
6	55.8	35.5	4.17	13.5
7	59.6	34.2	5.54	13.4
8	59.4	35.0	5.12	13.0
9	61.1	34.8	5.3	12.3
10	60.7	34.4	4.9	11.9
11	59.2	35.3	4.1	11.2
12	61.0	33.5	5.2	11.0
13	60.9	34.9	4.5	10.7
14	60.6	33.5	4.5	9.6
15	62.7	31.8	5.2	8.3
16	62.6	32.3	4.6	7.6
17	60.3	38.9	0.7	6.6
18	62.4	34.6	2.7	5.6
19	64.3	30.5	4.8	5.3
20	60.7	38.6	0.4	5.2
21	60.6	38.1	0.5	5.1
22	62.6	38.5	0.8	5.0
23	61.0	35.7	0.8	3.3
24	64.6	34.6	0.7	0.1

*Combined.

The examples of Table I have been listed in the declining order of Deposition Factor (D/F). Analysis has shown that for application of the present invention to critically dimensioned components such as jet engine parts, it is necessary to maintain the weight gain resulting from coating application processing at a reasonably low level. As shown by the Table II, a Deposition Factor of about 17 results, unexpectedly, in almost twice the weight gain compared with a Deposition Factor of about 16. Thus, a preferred aspect of the present invention limits the composition of the ternary powder used in the method of the present invention to a Deposition Factor of about 16 or less.

TABLE II.—PROCESSING EFFECT

Example	D/F	Wt. gain (mg./cm.^{2})
1	17.2	27.2
2	15.7	15.6
3	14.3	12.4
5	13.6	11.0
8	13.0	12.3
9	12.3	9.4
10	11.9	8.4
12	11.0	6.5
13	10.7	6.0
14	9.6	5.1
15	8.3	6.0
16	7.6	5.2
18	5.6	5.5
19	5.3	6.0

The specific method used to obtain the data of which Table II is typical included use of a pack mixture of about 40% of the ternary alloy shown and about 60% of Al_2O_3 powder to which had been added about 0.2 weight percent of NH_4F powder as an activator. The specimens treated were of a nickel base superalloy sometimes referred to as René 41 and having a nominal composition, by weight, of 19% Cr, 11% Co, 10% Mo, 3% Ti, 1.5% Al, 0.1% C, 0.005% B with the balance essentially Ni and incidental impurities. After surface cleaning, the specimens were placed in a small coating box and surrounded with the particulate pack mixture. The coating box was then placed in a retort located in a furnace preset at 1950° F. After purging the retort and coating box with argon, a hydrogen atmosphere was introduced and the coating box was kept at 1950° F. for about 4 hours. Then it was pulled back into the cold zone of the retort where it was allowed to cool to 300° F. The retort was then opened and the coating box was removed.

As can be seen from Table II, those ternary alloys having a Deposition Factor of up to about 11 resulted in a relatively uniform weight gain. However, those ternary alloys having a Deposition Factor of between about 11 and 16 showed a slowly increasing weight gain rate. Above about 16, the weight gain rate became extremely rapid.

As was indicated above, the Deposition Factor associated with the present invention is a measure of the aluminum in excess of the sum of the amount which will form the stoichiometric compound AlTi in the matrix and the amount necessary to form the complex carbide Ti_2AlC, in that preferred form of the present invention in which the matrix is a binary of Ti and Al, with the nonstoichiometric Ti being in the gamma form. As will be pointed out later in connection with the drawing, this preferred form avoids the formation of substantial quantities of $TiAl_3$ which can, under certain compositional conditions, precipitate in the gamma Ti of the matrix.

The Deposition Factor, D/F, is a dimensionless number related to the present invention's recognition of the unique interaction of carbon with the aluminum and titanium. Thus the Deposition Factor is a mathematical tool which physically defines this unique interaction considering the effective amount of carbon as that in the combined state in the form of a complex carbided Ti_2AlC. The Deposition Factor, which is a measure of excess aluminum as described above, can be derived or explained mathematically as follows:

$$\mathrm{Ti}_{(\mathrm{alloy})}-\mathrm{Ti}_{(\mathrm{Ti_2AlC})}=\mathrm{Ti\ free\ for\ matrix}=X$$

(1)

$$X=\mathrm{Ti}_{(\mathrm{alloy})}-\left(\frac{47.90\times 2}{12.01}\right)\mathrm{C}$$

(2) $$\mathrm{Al}_{(\mathrm{alloy})}-\mathrm{Al}_{(\mathrm{Ti_2AlC})}=\mathrm{Al\ free\ for\ matrix}=Y$$

$$Y=\mathrm{Al}_{(\mathrm{alloy})}-\left(\frac{26.98}{12.01}\right)\mathrm{C}$$

(3) Equivalent gram atomic weight of Al to form TiAl=Z

$$Z=\left(\frac{26.98}{47.90}\right)X$$

(4) $\mathrm{D/F}=Y-Z=\mathrm{Al}+2.25\ \mathrm{C}-0.562\ \mathrm{Ti}$

where Al, C and Ti are in weight percent and C is carbon combined in Ti_2AlC and not total carbon.

Once the specific area of the phase relationship, shown in and described later in connection with the drawing, has been established, the Deposition Factor can be approximated from:

$$\mathrm{D/F}=\mathrm{Al}+2\mathrm{C}-\frac{\mathrm{Ti}}{2}$$

The D/F number, representing a materials balance, for positive numbers defines the aluminum in the matrix in excess of the TiAl stoichiometric composition. Hence it represents the excess aluminum which is available for coating deposition. When the D/F number reaches zero, there is no excess aluminum over the amount of Ti in the matrix and the remaining phases are Ti_2AlC and stoichiometric TiAl. At such a point, with a properly activated ternary alloy as described above, equal numbers of aluminum and titanium atoms will be deposited in the same manner. If the D/F number is less than zero, there is an excess of Ti and deposition of Ti will become even more pronounced. Thus it is possible to control, through the present invention, the deposition of either aluminum, or titanium, or combinations of the two.

These various phases and relative depositions of aluminum and titanium will be more readily understood by reference to the drawing. Using the Deposition Factor relationship described above, a series of D/F numbers were calculated for various Ti-Al-C ternary alloy compositions. As shown in the drawing, the D/F numbers were then plotted against the aluminum content of the alloy for carbon contents in the range between zero to 10 weight percent.

During the evaluation of the present invention, it has been shown that a great many compositions varying in amounts of Ti, Al and C, but having the same D/F number, were found to behave substantially identically during a given treatment cycle for a particular alloy surface. It was recognized that regardless of the aluminum content of the ternary alloy, the available aluminum for deposition will always be the same if the D/F numbers are equal. Similarly, this type of plot can be used to find D/F numbers of ternary alloy powders for the practice of the present invention if the Al and C concentrations are known. An evaluation of a variety of ternary alloy powders of Ti, Al and C coupled with their physical behavior, allowed construction of the phase boundary lines presented in the drawing.

During an evaluation of the wide variety of alloys on which the drawing is based, it was recognized that those ternary alloys having a D/F number less than zero, and hence lying within the area AGHBA, include Ti in the matrix in the alpha condition and have an excess of titanium rather than aluminum. Surfaces or coatings produced from these alloy forms can be useful in certain instances. However, the oxidation and hot corrosion resistance is less than that produced from alloys found to the right of vertical line AB, in which area gamma titanium is formed. Therefore, in its preferred form, the present invention defines the D/F number as being greater than zero. In addition, it was found that a phase change occurs in the area of a D/F number of about 18. This change is represented in the drawing by broken line CD. Above that area, the matrix can include substantial amounts of $TiAl_3$ which tends to produce coatings of excessive thicknesses. Therefore, the specifically preferred form of the present invention defines the D/F number as being between zero and about 18.

It was found that the matrix in the area AIFA is predominantly aluminum and that only aluminum will be deposited at a relatively high rate from such a system. Because the present invention has as one of its principal objects the provision of an improved surface treatment which substantially maintains the original dimensions of the article being treated, the rapid deposition of aluminum, though useful in certain instances, is not specifically preferred for jet engine components. Therefore, the specifically preferred form of the present invention contemplates the use of ternary alloy of Al, Ti and C within that area of the drawing defined by ABCDA, having a composition by weight of about 50–70% Ti, 20–48% Al and 0.5–9% C (combined) and a D/F number of between zero and about 18.

As was mentioned above, carbon plays a significant role in the ternary alloy of the present invention. For instance, when the ternary alloy of Example 20, having an actual combined carbon content of 0.35% was used to coat a specimen of the type and in the manner described above, the resulting coating included relatively large amounts of titanium and had relatively low oxidation and hot corrosion resistance. A similar investigation in connection with the alloy form of Example 1, having a combined carbon content of about 9% and a total carbon content of about 12%, disclosed the beginning of the formation of high concentrations of the undesirable $TiAl_3$. The undesirable TiC also was present. Subsequent coating evaluations made with powders from Example 1 alloy showed a very high rate of coating deposition, resulting in excess thickness. This rapid weight gain, shown in Table II, indicates a different kind of mechanism beginning to occur at D/F numbers greater than about 16. This is believed to be associated with such compounds as $TiAl_3$ in the matrix. Hence the preferred form of the present invention avoids the ternary alloy of Ti, Al and C which will form substantial amounts of $TiAl_3$.

As shown by the drawing and for these reasons, the range of combined carbon in such ternary alloys is limited to about 9 weight percent. With at least about 0.5 weight percent carbon present, aluminum is preferentially deposited along with some titanium. With lesser amounts of carbon or in the absence of carbon, substantially equal amounts of titanium and aluminum appear to be deposited. Because larger amounts of titanium, such as would occur in this latter instance, can have deterimental effects on oxidation and hot corrosion resistance of the resulting coating, the present invention requires the presence of carbon combined as described above within a critical range.

Specimens of the above described René 41 to which the ternary alloys of Table I had been applied by the specific method previously described, were tested under oxidizing conditions at 2050° F. for 23 hours. Photomicrographic studies of the specimens after testing showed that the inner diffusion zone of the specimens coated with powders having a low D/F number, such as Examples 16 and 18, seemed to dissolve more extensively than those coated with high D/F number powders, such as Examples 1 and 7. In the case of specimens coated with the powder of Example 1 having a D/F number of about 17, undesirable diffusion voids in the inner diffusion zone were observed. Such voids, when continuous, can cause the coating to spall. Also, they can become natural sites for high stress concentrations which develop cracks leading to early fatigue failures. Thus, both from the standpoint of coating deposition range and coating integrity, the preferred form of the present invention defines a ternary powder having a Deposition Factor of about 16 or less.

Coatings produced from ternary alloys of Table I having a Deposition Factor between about 3 and 16 resulted in relatively low titanium content. However, coatings resulting from the use of the ternary alloy powders having a D/F number of close to or below zero resulted in relatively high titanium concentrations in the coating. Oxidation testing of the specimens coated with the ternary alloys of Table I showed a gross failure in the coated specimens with high titanium concentrations whereas the coatings having lower titanium concentrations showed no indication of oxidation attack even though the coatings were of equal thickness and were exposed to the same oxidation parameters.

It is believed that coatings of the type to which the present invention relates and with higher titanium concentrations, when applied to nickel base superalloys exhibit poor oxidation resistance as a result of the formation of a poor oxidation resistant titanium-rich $Ni_3(Al, Ti)$ phase in the outer coating layer. The preferred compounds in such coating are NiAl or Al-rich NiAl which have excellent resistance to high temperature oxidation. Through tests of this nature, it has been found that when the D/F number of a ternary alloy powder within the composition range of the present invention reaches the value of zero, the powder has reduced its effectiveness as a coating medium to produce highest quality oxidation resistant coatings. This will be shown later to be particularly true with respect to the coating of surfaces of a material based on cobalt.

As was stated above, it has been found that the titanium content of the coating produced according to the present invention increases with decreasing D/F numbers. Oxidation tests at 1050° F. for 23 hours were conduced one specimens of the above described René 41 alloy using the ternary alloy of Examples 4, 5 and 18 of Table I. The results showed that oxidation failure of such coating will occur on certain nickel base superalloys through the use of such ternary alloy powders having a D/F number below about 5. For example, a pack mixture including the ternary alloy of Example 18, having a starting D/F number of 5.6, was used in repeated applications which decreased the D/F number through use to 2.8 and then to 0.6. Oxidation failure of the coating, which occurred at a D/F number of 2.8, is believed to be the result of the coating's higher titanium content forming the lower oxidation resistant Ti-rich $Ni_3(Al, Ti)$ phase. However, in another similar evaluation when the powder of Example 4 was applied repeatedly, thereby decreasing its D/F number from 13.7 to 10.2 to 9.2, the oxidation characteristics of the applied coating remained substantially the same and no oxidation failure was observed. Similarly, the alloy powder of Example 5 of D/F number 13.6 through application was reduced to 12.0 and then to 10.4. The resultant coating showed no substantial decrease in oxidation resistance. It is interesting to note that photomicrographic studies of the oxidation sample of Example 5, reduced through usage to a D/F number of 10.4, appears almost identical to the oxidation sample of Example 4 having a D/F reduced to 10.2 through use, even though the two ternary alloys used in the pack mixture had different compositions within the range of the present invention.

Whereas the above described coatings on nickel base alloys consist mainly of NiAl(Ti), the coating formed on a cobalt base alloy using the same powders and processing parameters consists mainly of CoAl(Ti). As was pointed out above, the NiAl compound has excellent oxidation resistance. However, as the Al is replaced by Ti, the resistance to oxidation tends to decrease. This becomes even more evident as the Ti replaces the Al in CoAl in cobalt base alloys such as one consisting nominally, by weight, of 25% Cr, 10% Ni, 7.5% W, .5% C with the balance Co, sometimes referred to as X–40 alloy. This decrease in oxidation resistance is based on the fact that cobalt-titanite (CoTi) is a relatively poor oxidation resistant compound compared with CoAl which is extremely oxidation resistant.

Therefore, the presence of a heavy titanium concentration in such coated cobalt base alloys is undesirable although a small amount of titanium is necessary for good hot corrosion (sulfidation) resistance. Evaluation of the present invention included application of various ternary alloy powders of Table I to X–40 cobalt base alloy specimens in the manner described above in connection with nickel base alloys. For example, the evaluation of the powder of Example 18, having a D/F number of 5.6 and excessive concentrations of Ti in the coating in the form of CoTi resulted in coating failure during oxidation testing. Other specimens coated with powders having D/F numbers of 13.6 (Example 5) and 13.7 (Example 4) showed no evidence of oxidation failures even after several reuses which would reduce the D/F number substantially.

From oxidation and hot corrosion evaluation as well as phase studies as described above, it was recognized that the present invention when applied to surfaces based on cobalt is preferably confined to the use of a powder consisting essentially of, by weight, 59–62% Ti, 32–35% Al and 4.5–6% combined carbon. The Deposition Factor number is preferred in the range of 9–16 to control the amount of titanium in the coating and to limit the precipitation of the undesirable $TiAl_3$ to concentrations which have been found to be acceptable from the coating thickness viewpoint.

As has been described above, the Ti-Al-C ternary alloy in which this invention requires the presence of the complex carbide Ti_2AlC, is useful in certain applications, for example on nickel base superalloys as the above described René 41 alloy, when the ternary alloy combined carbon range is about 0.5–3. However, because coating thickness has been found to be affected by combined carbon content, the resultant coatings are generally too thin for adequate resistance to stringent oxidation and hot corrosion conditions. Therefore, a preferred form of the present invention for application to nickel base alloys for severe hot oxidation conditions employs the ternary alloy having a composition, by weight, of 60–63% Ti, 32–35% Al and 3.5–5% combined carbon, with the Deposition Factor maintained in the range of about 9–13.

As was mentioned before, certain amounts of uncombined carbon, for example, up to 3 weight percent or more can be present without detrimental effect on the ternary alloy. In addition, small amounts of such impurities as Ni, Mn, Cr and Fe can be present in the total amount of about 2 weight percent.

One type of hot corrision evaluation of the coating resulting from the present invention was conducted in a dynamic oxidation flame tunnel provided with means to ingest a 1.6% $NaCl/Na_2SO_4$ salt solution and to produce a corrodent concentration of about 100 p.p.m. The $NaCl/NA_2SO_4$ ratio was 9:1, closely simulating the Cl/SO_4 ratio in sea water. One such test was conducted on the airfoil surface section of nickel base alloy jet engine turbine blades having a nominal composition, by weight, of 18% Cr, 3% Ti, 3% Al, 18% Co, 4% Mo, 0.005% B, 0.05% C, balance Ni and incidental impurities. The pack mixture used in the manner described above included the ternary alloy by weight of 62.0% Ti, 34.8% Al, 4.6% carbon, total, 0.16% carbon, free with less than 0.15% Fe. The alloy was mixed with powdered Al_2O_3 in an amount such that the ternary alloy consisted essentially of 40 weight percent and the Al_2O_3 powder consisted of about 60 weight percent of the pack mixture. To this mixture was added 0.2 weight percent NH_4F activator. Processing was conducted at 1950° F. for four hours. In addition, comparison testing was made with the same article coated with two commercially available high temperature pack diffusion type coatings currently used as a coating in production on jet engine turbine blade airfoils. After tests of 25 and 50 hours at temperatures ranging between 1600–1800° F. to simulate engine operation, corrosive attack was noticed on the airfoils coated with the known coatings, whereas the coating provided by the present invention was virtually unaffected. From comparison with control specimens, and from subsequent engine tests, it has been found that the hot corrosion flame tunnel tests closely simulates actual engine test. Thus, the present invention provides a surface treatment of improved hot corrosion resistance as well as normal oxidation resistance at elevated temperature.

The same specific pack mixture and application method described immediately above was used to apply a surface coating to an iron base alloy widely known and used as A.I.S.I. 321 stainless steel. The results were approximately the same as those obtained from the application of that material to the above described nickel base superalloy. Consequently the present invention is particularly useful in connection with the surface protection of those alloys based on the closely related transition triad eleemnts Fe, Co and Ni.

The particulate pack mixture of the present invention includes a powder of the multiphase ternary alloy of Ti, Al and C, as described above, in the range of 20–90 weight percent of the mixture; an inert filler material, to prevent powder sintering, in an amount of about 10–80 weight percent; and a halide salt activator, preferably one selected from the chlorides and fluorides of NH_4 and of the alkali metals in Group I-A of the Periodic Table of Elements. The use of certain of this class of activator in the range of about 0.2–10 weight percent of the mixture has been described in detail in the above identified copending application. The use of such halide salt activators as NaF, KF, NH_4Cl and NH_4F in pack mixtures described above have shown that range to be applicable to the present invention as well. In addition, the bromide and iodide forms of such salts were tested and found to be satisfactory, though more sluggish in action. Such halide salt activators as CrF, for example, in an amount of about 0.5% with the last described specific pack mixture, was shown to operate successfully as an activator in the present invention. In addition, it was found that good results can be obtained with the more reactive activators as NH_4Cl, KCl, NaCl and NH_4F, when included in the pack mixture at somewhat less than 0.2 weight percent. This amount, which is herein stated as about 0.1 weight percent, means a small but reasonably effective amount.

The halide salt activators in the range of about 0.1–10 weight percent can be included in the particulate pack mixture and in the practice of the method of the present invention. However, the more reactive activators of the type described above tend to perform their function of bringing about transfer of appropriate amounts of aluminum and titanium at a relatively low point in the useful range. A typical simplified mechanism for the coating of a nickel base alloy with aluminum from the ternary Ti-Al-C alloy using NH_4F as the halide carrier first involves the reaction to produce aluminum fluoride and the ammonium ion. Then there occurs a reaction with nickel in the surface of the nickel base alloy to form a nickel aluminum. The use of excessive amounts of activator can result in the transfer of too much titanium, thereby reducing coating oxidation resistance.

It has been found that with the more reactive activators, the rate of conversion of such elements as aluminum in the ternary alloy to the halogen prior to the reaction with the article surface increases in rate up to about 2% activator content in the pack. Thereafter, there is a much slower, if any, increase in rate. Usually, such a small rate increase would not warrant the inclusion of greater amounts of activator from a practical and economical viewpoint. Therefore, the preferred range for the inclusion of the reactive activators as NaF, KF, NH_4Cl and NH_4F is about 0.1–2 weight percent. In addition, although the preferred processing temperature is in the range of about 1600–2100° F., such as for about 1–4 hours, it has been found that the halide salt activators will react with an element of the ternary alloy at temperatures as low as about 1200° F.

Although the present invention in its various aspects has been described in connection with specific examples, it will be understood by those skilled in the arts, particularly metallurgy and coating, the variations and modifications of which the present invention is capable. It is intended in the appended claims to cover all such variations and modifications.

What is claimed is:

1. A ternary alloy powder particularly useful in a method for coating an article surface, the ternary alloy consisting essentially of, by weight:

about 50–70% Ti, 20–48% Al and 0.5–9% combined carbon,

the alloy having a dispersion of Ti_2AlC complex carbide in a matrix selected from the group consisting of Ti, Al and their alloys.

2. The alloy of claim **1** in which the matrix is a binary alloy of Ti and Al with the Ti in the gamma range of the Ti-Al phase diagram and having a Deposition Factor (D/F) number in the range of 0 and about 18 as determined by the relationship:

$$D/F = Al + 2C - \frac{Ti}{2}$$

in which the Al, Ti and C are in weight percent.

3. The alloy of claim **2** in which the elements lie within the area ABCDA of the drawing.

4. The alloy of claim **3** in which the elements consist essentially of, by weight, 59–62% Ti, 32–35% Al and 4.5–6% combined carbon with the Deposition Factor number in the range of about 9–16

5. The alloy of claim **3** in which the elements consist essentially of, by weight, 60–63% Ti, 32–35% Al and 3.5–5% combined carbon with the Deposition Factor number in the range of about 9–13.

References Cited

UNITED STATES PATENTS

3,052,538	9/1962	Jech et al. __________	75—175.5
3,203,794	8/1965	Jaffee et al. ________	75—175.5

FOREIGN PATENTS

220,571	1/1959	Australia.

OTHER REFERENCES

WADC Technical Report, 52–335, Titanium Phase Diagrams, Kessler et al, November 1953, pp. 45 and 54.

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