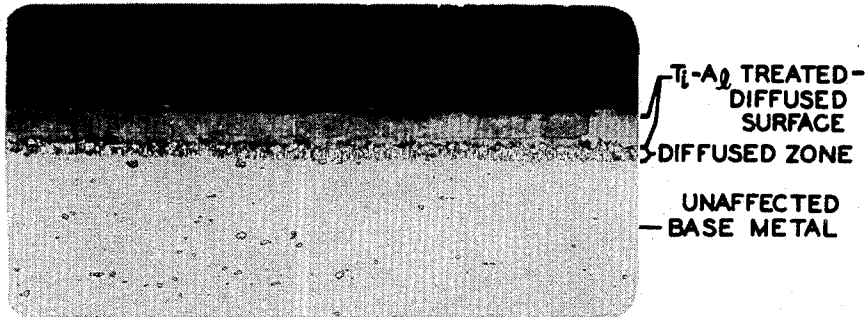


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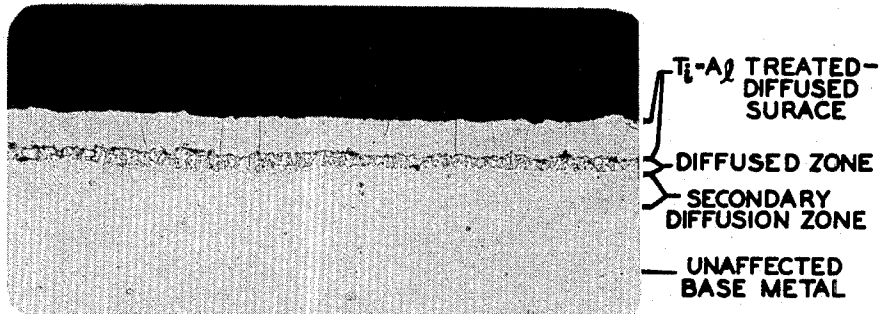
M. A. LEVINSTEIN ET AL  
METHOD OF CO-DEPOSITING TITANIUM AND ALUMINUM ON  
SURFACES OF NICKEL, IRON AND COBALT  
Filed Nov. 12, 1964

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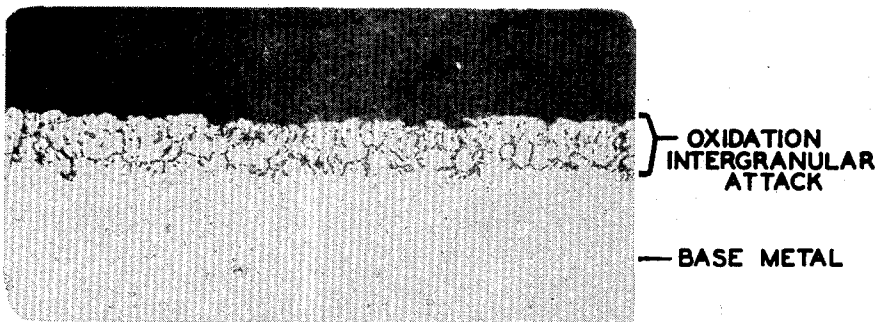
**Fig 1** SPECIMEN AS TREATED



**Fig 2** TREATED SPECIMEN AFTER 1800 °F CYCLIC OXIDATION



**Fig 3** UNTREATED SPECIMEN AFTER 1800 °F CYCLIC OXIDATION



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3,415,672

## METHOD OF CO-DEPOSITING TITANIUM AND ALUMINUM ON SURFACES OF NICKEL, IRON AND COBALT

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Filed Nov. 12, 1964, Ser. No. 410,645

9 Claims. (Cl. 117—71)

### ABSTRACT OF THE DISCLOSURE

The method for treating a metallic surface of a material based on iron, nickel or cobalt involves co-depositing Ti and Al in a non-oxidizing atmosphere onto such surface from a binary Ti-Al alloy in the vapor state through such a halide salt activator as NaF, KF and  $\text{NH}_4\text{Cl}$ .

This invention relates to the treatment of metallic surfaces, and more particularly, to the treatment with a binary Ti-Al alloy of metallic surfaces based on alloys of iron, nickel and cobalt.

Components of modern power producing apparatus, for example turbine components of jet engines, are exposed to temperatures in the range of 1800° F. or above in the presence of oxidizing atmospheres. Such components, generally manufactured from temperature resistant iron, nickel or cobalt base alloys known as "superalloys," are expected to operate without significant loss in cross-section for a minimum of 150 hours. Such a performance cannot be obtained unless these superalloys are shielded from oxidation and erosion by protective coatings or surface treatments.

Coatings or protective surfaces employed must, of course, protect the base metal. However, they must not weaken nor contribute any deleterious effect to it. In applications relating to flight, design requirements of components place severe restrictions on weight. Consequently, strict limitation is placed on coating thickness.

A wide variety of coatings of the type which add to the dimensions and weight of an article have been reported. For example, many varieties applied by electrodeposition, molten baths, flame spraying, cladding and similar procedures, singly or in various combinations are well known. While some coatings of these types can withstand the desired operating conditions, they nevertheless change the finished dimensions and add to the weight of the article. In addition, known coatings and surface treatments are difficult or impossible to apply in small passages within articles. Furthermore, the edge thickening effects and the clogging of narrow openings or passages have been troublesome with known coatings. For example, the use of molten bath type processes results in excessive surface build-up and blockage of narrow passages. Cladding is difficult, costly and cannot be used to cover narrow passages. Electrodeposition cannot plate in narrow passages and electroless deposition has thermal limitations. Relatively poor control over some pack cementation type processes results in undesirable coating properties and characteristics.

Therefore, it is a principal object of the present invention to provide for a superalloy surface an improved treatment method which substantially reproduces the original dimension and surface finish prior to treatment yet which provides protection for article surfaces based on iron, cobalt or nickel base alloys in the temperature range of 1800° F. and above for a minimum of 150 hours in air.

Another object is to provide for a superalloy surface an improved treatment method which can be applied to superalloy articles having small passages or openings such that

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the openings are not clogged in processing and that the treatment method functions within the openings and passages as well as on the other surfaces of the article.

Still another object is to provide an article having an improved surface, resistant to oxidation conditions at temperatures of about 1800° F. and above with little, if any, addition of weight.

These and other objects and advantages will be more clearly understood from the following detailed description, examples and drawing which are meant to be exemplary of rather than any limitation on the scope of the present invention.

In the drawing:

FIG. 1 is a photomicrographic view including a surface treated according to this invention taken prior to oxidation testing;

FIG. 2 is a photomicrographic view including the surface of FIG. 1 taken after oxidation testing; and

FIG. 3 is a photomicrographic view of untreated base metal after oxidation testing.

Briefly, in its broader aspects the present invention provides a method for treating a metallic article surface based on a metal from the group iron, nickel and cobalt substantially to reproduce the original dimensions and surface finish while providing an oxidation protective surface. The method includes the step of codepositing titanium and aluminum onto the article surface in a nonoxidizing atmosphere from a vapor state of a binary titanium-aluminum alloy consisting essentially of, by weight, more than 15% and less than 50% aluminum, with the balance titanium, in the presence of a halide salt activator selected from the group NaF, KF and  $\text{NH}_4\text{Cl}$ .

In its preferred form, the present invention comprises, in a method for treating a metallic article surface based on the metal of the group iron, nickel and cobalt, the step of co-depositing titanium and aluminum onto the article surface in a non-oxidizing atmosphere and at a temperature of about 1750–2150° F. from a vapor state of a powdered binary titanium-aluminum alloy consisting essentially of about 30–35 weight percent aluminum with the balance titanium in the presence of a halide salt activator from the group NaF, KF and  $\text{NH}_4\text{Cl}$ .

The application of the combination of titanium and aluminum as a surface treatment or coating has been previously reported. For example, there are known molten bath applications and pack treatments, the latter with the titanium in the form of ferro-titanium or nickel titanium alloys including aluminum as well. However, the presence in the treated surface of a material such as iron, nickel, manganese, silicon and the like prohibits close control of treatment of the surface or coating. It has been found that the use of a binary Ti-Al alloy within a specified composition range and a particular group of halide salts affords unexpected accuracy in treatment control while affording improved oxidation resistance. Therefore the present invention specifically avoids the inclusion of elements other than aluminum and titanium in the vaporized alloy in order to accurately control the extent of surface treatment.

From this unexpected finding, it would appear as if a coating of any desired composition could be produced by a pack-cementation process. It is believed, with regard to the present invention, that the two elements of the coating, titanium and aluminum when placed in a pack with a suitable activator at high temperatures will react with the activator to form the metal halides. The halide gases, in turn, are believed to decompose and deposit a metal or alloy on the surface to be treated. The temperature at which the method of the present invention is conducted, is between 1750° F. and the temperature above which the base metal is undesirably affected. Generally and practically, this range is about 1750–2150° F. Penetration of

the base metal by the deposited metal produces a surface through which the deposited metal has diffused.

It would seem, superficially, that this process could be generally predicted from knowledge of the characteristics of halide salts and their reactions with metals, as well as the diffusion rates of metals and alloys one into the other. However, this is not so for there are a number of significant deviations which can be expected to prohibit prediction of the present invention. Assuming ideal thermodynamic behavior throughout, it might appear capable of hypothesis that the composition of the composite will be controlled by the composition of the gaseous halide mixture. This mixture is determined by the concentration of each coating constituent in the pack. On closer examination, deviation from ideality can be expected to be considerable.

With regard to the gaseous metal halide generated from the alloys of the specific compositions, as the energy of formation of any metal halide differs from that of the other, and titanium and aluminum solutions are not ideal, the compositions of the mixture of halide gases produced from interaction of halogens with such alloys will not be proportional with that of the solid mixture. Any estimate of the ultimate coating composition will be uncertain from this effect alone. But gas composition is not the only factor which will have a large effect on the nature and composition of any coating. Among these are the kinetics of pyrolysis of each of the gaseous species, the free energy of interaction of deposited metal with the substrate and the diffusion characteristics of each deposited metal when in the presence of the other.

It has been found, however, that the method of the present invention including the use of a binary alloy consisting of greater than 15 and less than 50 weight percent aluminum, with the balance titanium, in the presence of a halide salt selected from NaF, KF and  $\text{NH}_4\text{Cl}$  when heated together within the range of 1750–2150° F. in a non-oxidizing atmosphere, results in an easily controlled oxidation resistant coating particularly for that group of alloys known as the "superalloys." In subsequent examples, it will be shown that this particular selection of halogen salts can be used in the practice of the present invention. However, such halogen salts as NaCl, KCl, the iodides and the bromides have been tested and, though closely related to the halides used in this invention, they do not function adequately as activators in the practice of the method of the present invention.

The method of the present invention involves the co-deposition of aluminum and titanium from a binary Ti-Al alloy first converted to its vapor state prior to deposition and through the use of a halide salt activator selected from  $\text{NH}_4\text{Cl}$ , NaF and its closely related compound KF. It has been found that this type of co-deposition can best be accomplished with the binary alloy in powdered form and in the well known process involving fluidized beds or the pack cementation type process. Of these two, the pack process is the most economically conducted and was generally used in the study of the present invention.

#### EXAMPLE 1

Specimens of a nickel base superalloy having a nominal composition, by weight, of 0.15–0.20% C, 8–11% Cr, 4.5–5.0% Ti, 5–6% Al, 13–17% Co, 2–4% Mo, balance Ni, were in the form of cast flat specimens and of test bars, the latter being the conventional 0.252 cylindrical type with threaded shanks for tensile testing. A binary 35 weight percent aluminum, 65 weight percent titanium alloy was cast and reduced in a crusher until particles of size —100+200 were obtained. A powdered pack mixture was made with the following ingredients in percent by weight:

50% alumina  
40% binary Ti-Al alloy  
10% sodium fluoride activator

The alumina mesh size was —150+200. The pack composition was mixed thoroughly for several hours in a blender prior to introduction of the mixture into a retort in which the specimens were placed. Prior to placement of the specimens in the retort, they were vapor blasted, washed with water and rinsed with acetone. After placing the specimens in the retort with the pack composition, the retort was sealed, evacuated and back filled with argon. The retort was placed in a furnace in which the internal temperature of the retort was allowed to reach 1775° F. where it was maintained for 1 hour. The retort was then cooled rapidly to about 1400° F. in about 10 minutes then the retort was opened and the specimens were removed. The surface of the specimens were uniformly treated with a thickness change of no more than 0.0005" per side.

The high degree of control of treated surface thickness is achieved by the present invention through the co-deposition from a vapor state of a titanium-aluminum binary alloy containing aluminum in excess of 15% and less than 50% by weight with the balance titanium; conducted in a non-oxidizing atmosphere. The following Table I compares treated surface conditions with the binary alloy used in the co-deposition onto a nickel base superalloy having a nominal composition, by weight, of 19% Cr, 11% Co, 10% Mo, 3% Ti, 1.5% Al, 3% Fe with the balance nickel sometimes referred to as René 41 nickel base alloy.

TABLE I.—SURFACE CONDITION COMPARISON

| Binary Alloy | Wt. Percent |    | Remarks                                                    |
|--------------|-------------|----|------------------------------------------------------------|
|              | Al          | Ti |                                                            |
| A.....       | 10          | 90 | Very slow deposition.                                      |
| B.....       | 15          | 85 | Poor reproducibility.                                      |
| C.....       | 30          | 70 | Uniform coverage, good deposition rate, easily controlled. |
| D.....       | 35          | 65 |                                                            |
| E.....       | 50          | 50 |                                                            |

The binary alloys of Table I were used in the pack process described in Example 1 above at a temperature of about 1775° F. for about 1 hour in an argon atmosphere.

The use of binary alloys A, B and E of Table I resulted in unsatisfactory surface conditions because of poor reproducibility or very slow deposition (alloys A and B) or because of a wide variation in thickness, too thick a coating and excess aluminum in the coating (alloy E). On the other hand, the use of alloys C and D within the preferred range of about 30–35 weight percent aluminum, with the balance titanium resulted in a uniform, easily controlled surface treatment with no more than about 0.001" total change in thickness. Furthermore, alloys C and D had the ability, in the method of the present invention, to penetrate and coat narrow internal passages and openings in articles.

The procedure of Example 1 was repeated with variations in the composition of the binary alloy added to the pack. The results with regard to weight change and thickness change are shown in Table II.

TABLE II

| Binary Alloy (wt. percent) |    | Treatment Time (hrs.) | Weight Change (mg./cm. <sup>2</sup> ) | Thickness Change (mil./side) |
|----------------------------|----|-----------------------|---------------------------------------|------------------------------|
| Al                         | Ti |                       |                                       |                              |
| 35                         | 65 | 1                     | 2.2                                   | 0.2                          |
| 35                         | 65 | 1                     | 2.0                                   | 0.4                          |
| 35                         | 65 | 1                     | 1.8                                   | 0.1                          |
| 35                         | 65 | 1                     | 2.0                                   | 0.3                          |
| 35                         | 65 | 4                     | 5.4                                   | 0.5                          |
| 35                         | 65 | 4                     | 5.1                                   | 0.5                          |
| 35                         | 65 | 4                     | 5.4                                   | 0.5                          |
| 35                         | 65 | 4                     | 5.1                                   | 0.5                          |
| 90                         | 10 | 1                     | 17.1                                  | 2.0                          |
| 90                         | 10 | 1                     | 19.7                                  | 1.3                          |
| 90                         | 10 | 1                     | 14.3                                  | 2.1                          |

It should be noted that the binary alloy form of 35 weight percent aluminum–65 weight percent titanium showed a very uniform rate of deposition and a change

in thickness per side of less than 0.0005". This was true even after 4 hours of treatment. On the other hand, the 90% Al-10% Ti alloy showed a significantly larger weight gain during processing with a significantly larger and undesirable change in dimensions.

Subsequent specimens prepared with holes of 5, 10 and 15 mils in diameter from the same material were processed as in Example 1. Not only was the exterior of the specimens coated uniformly but also the interior walls of the passages were coated uniformly without clogging the holes.

#### EXAMPLE 2

Specimens in the shape of an airfoil to simulate a vane portion of a blading member, such as an axial flow compressor blade, were made from 0.060" sheets of the above described René 41 nickel base superalloy. The specimens were vapor blasted with 400 mesh alumina and rinsed with acetone. The binary Ti-35% Al alloy powder of Example 1 was used in the powdered pack mixture which had the following ingredients in percent by weight:

60% alumina  
38% binary Ti-Al alloy  
2% anhydrous NaF activator

Prior to placing the specimens in the retort with the powdered pack mixture as in Example 1, an aluminum oxide slurry blanket or barrier was applied to the specimen surface in order to prohibit adherence of the pack mixture to a surface of this type of an alloy. The  $Al_2O_3$  barrier or blanket was applied by dipping the specimens in a slurry having the following composition:

70 grams methylcellulose  
805 grams of 150 mesh aluminum oxide  
670 grams of distilled water

After dipping in the slurry the specimens were placed in an oven and baked for 2 hours at 270° F.

Mo, 3.5% Ti, 2.9% Al, 0.1% C, up to 4% Fe, with the balance Ni was used as specimen material in this example. Cast specimen strips of approximately 0.070" x 0.375" x 2.0" were polished flat and were washed and dried as in Example 1 before placement in the pack. Measurement of thickness and weight of specimens were made before and after treatment in order that the weight gain of diffused material could be determined. The specimens were treated as in Example 2, using an aluminum oxide barrier between the specimens and the pack mixture.

TABLE III  
[Weight gain (mg./cm.<sup>2</sup>)]

| Alloy          | Activators               |                          |                          |
|----------------|--------------------------|--------------------------|--------------------------|
|                | NaCl                     | NaF                      | NH <sub>4</sub> Cl       |
| 35Al-65Ti----- | 1.1<br>0.4<br>0.7<br>0.5 | 2.9<br>2.1<br>2.7<br>2.6 | 3.5<br>5.6<br>3.9<br>4.0 |
| 63Al-37Ti----- | 0.1<br>0.2<br>0.3<br>0.1 | 6.0<br>5.4<br>4.4<br>7.1 | 7.3<br>7.7<br>8.1<br>9.3 |

The above Table III shows that for NaF, the amount of coating deposited increases with aluminum content of the titanium-aluminum alloy but not proportionally. For NaCl, the data is scattered indicating either the formation of the metal chloride gas or that the decomposition energy of the chloride may be the limiting factor. However, the NH<sub>4</sub>Cl data indicates the critical factor is the rate of formation of the metal halide.

The six combinations of metal alloys and activators were exposed to a cyclic oxidation test for 150 hours at 1800° F. in a flame tunnel with a one minute cooling and heating cycle between 1800° F. and 1000° F. every thirty minutes. The following Table IV compares the oxidation resistance of the six combinations after such tests.

TABLE IV.—THICKNESS AND OXIDATION RESISTANCE

|                | NaCl                  |                      | NaF                   |                      | NH <sub>4</sub> Cl    |                      |
|----------------|-----------------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|
|                | Thickness gain (mils) | Oxidation resistance | Thickness gain (mils) | Oxidation resistance | Thickness gain (mils) | Oxidation resistance |
| 35Al-65Ti----- | 0.7                   | Failed-----          | 1.0                   | Excellent-----       | 2.2                   | Good.                |
| 63Al-37Ti----- | 0                     | -----do-----         | 1.3                   | Some attack-----     | 2.4                   | Do.                  |

After this pretreatment, the specimens were placed in the retort with the pack mixture and the retort was closed, evacuated and back filled with argon. The retort was placed in a furnace at 2150° F. under a retort pressure of 5-10 p.s.i. of argon. The furnace temperature was adjusted to maintain the temperature inside the retort at 1950° F. where it was held for 3 hours. Then the retort was cooled to 1400° F. in about 10 minutes after which the specimens were removed from the retort. Because such heating removed the methylcellulose binder and water from the alumina blanket surrounding the specimens, the alumina was easily brushed from the surface of the specimen.

#### EXAMPLE 3

Binary compositions corresponding to TiAl and TiAl<sub>3</sub>, representing two eutectic alloys of titanium and aluminum were selected and prepared by first reducing to chips and then ball milling to approximately 100 mesh for incorporation into the powdered pack mixture of Example 1. These two binary alloy compositions in percent by weight are as follows: 35 Al-65 Ti and 63 Al-37 Ti. Each of these compositions was deposited in the presence of activators NaF, NaCl and NH<sub>4</sub>Cl. A nickel base alloy having a nominal composition, by weight, of 19% Cr, 19% Co, 4%

Tables III and IV show that the 35 Al-65 Ti binary alloy, particularly using NaF as the activator, produced coatings of uniformity, excellent oxidation resistance and good surface treatment thickness. However, it is to be noted that NaCl when used as an activator does not result in a satisfactory coating of adequate oxidation resistance.

Coatings from the 63 Al-37 Ti binary alloy were coarse, irregular and exhibited excessive diffusion characteristics in the oxidation tests. On the other hand, the 35 Al-65 Ti binary alloy showed less than 0.4 mil secondary diffusion in the oxidation tests. This is more clearly shown in Table V below. The 35 Al-65 Ti binary alloy was studied further with regard to oxidation resistance using NaF as an activator. The results of these studies are shown in the following Table V.

TABLE V.—CYCLIC OXIDATION RESISTANCE OF 35Al-65Ti WITH NaF ACTIVATOR  
[150 hrs. Cycled to 1,800° F.]

| Specimen Number | Wt. Gain (mg./cm. <sup>2</sup> ) | Specimen Thickness increase (mil/side) | Secondary Diffusion (mil/side) |
|-----------------|----------------------------------|----------------------------------------|--------------------------------|
| 1-----          | 0.27                             | 0.5                                    | 0.2                            |
| 4-----          | 0.33                             | 0.3                                    | 0.4                            |
| 5-----          | 0.18                             | 0                                      | 0.2                            |
| 8-----          | 0.41                             | 0                                      | 0.1                            |

After successful testing in this series, the surface was in excellent condition and the base metal was well protected. The oxidation behavior of this binary alloy was particularly gratifying. Table V lists the small weight gain, small dimensional changes and very small degree of secondary diffusion. Even though the oxidation resistance tends to be enhanced by the presence of a thicker treated portion, nevertheless even at a treatment thickness of 0.8 mil more particularly shown in the Table VI below, the coating provided good protection for at least 150 hours at 1800° F. The small secondary diffusion is quite important because it shows that the presence of titanium with aluminum is sufficient to inhibit the diffusion of aluminum. This result was not expected and could not be predicted because it was believed prior to this that the function of the titanium in a Ti-Al system was as a barrier to the diffusion of aluminum into the base metal. These data indicate that the mere presence of titanium in the proper proportions is enough.

Reproducibility runs were made with the cast specimens of the same length, width and thickness described above, polished flat and parallel within 0.0005". The results of this testing are shown in the following Table VI.

TABLE VI.—REPRODUCIBILITY OF 35Al-65Ti WITH NaF ACTIVATOR

| Specimen Number | Weight Gain (mg./cm. <sup>2</sup> ) | Thickness Change (mils) |         |
|-----------------|-------------------------------------|-------------------------|---------|
|                 |                                     | Specimen                | Coating |
| 1-----          | 2.7                                 | None                    | 0.8-1.0 |
| 2-----          | 2.3                                 | None                    | 0.7-0.8 |
| 3-----          | 2.2                                 | None                    | 0.8-0.9 |
| 4-----          | 2.2                                 | None                    | 0.8-0.9 |
| 5-----          | 2.1                                 | None                    | 0.8-1.0 |
| 6-----          | 2.0                                 | None                    | 0.7-0.8 |
| 7-----          | 2.1                                 | None                    | 0.6-0.8 |
| 8-----          | 2.0                                 | None                    | 0.6-0.8 |

The condition of the treated specimen of Example 2 before the above described cyclic oxidation treatment is shown in the photomicrograph of FIG. 1 at a magnification of 250X. FIG. 2 shows the excellent condition of that same specimen after 100 hours cyclic oxidation testing and FIG. 3 shows the oxidation intergranular attack and alloy depleted condition of the surface of an untreated specimen after 100 hours of the same oxidation testing. These specimens were etched with 3% H<sub>2</sub>O<sub>2</sub>.

#### EXAMPLE 4

Specimen buttons 5/8" in diameter and 0.25" thick made from a cobalt base alloy having a nominal composition, by weight, of 0.5% C, 25% Cr, 10% Ni, 8% W with the balance Co were prepared as in Example 1, and placed in a retort with a powdered pack mixture of the following ingredients in percent by weight:

59.8% alumina  
40% 35 Al-65 Ti binary alloy  
0.2% NH<sub>4</sub>Cl

The same procedure was followed as in Example 1 except that the temperature within the retort was maintained at 1950° F. for 3 hours. Upon removal and subsequent testing, the cobalt base alloy specimens were found to have the same surface uniformity and oxidation resistance as was indicated in the examples above.

#### EXAMPLE 5

Specimens 1/8" in diameter and 1" long made from an iron base alloy having a nominal composition, by weight, of 0.8% C, 4.1 Cr, 1.1% V, 4.25% Mo with the balance Fe were prepared as in Example 1 and placed in a retort with a powdered pack mixture of the following ingredients in percent by weight:

58% alumina  
40% 35 Al-65 Ti binary alloys  
2% NaF

The same procedure was followed as in Example 1 except that the temperature within the retort was maintained at 1750° F. for 1/2 hour. Upon removal and subsequent testing, the iron base alloy specimen was found to have an excellent surface treatment and to have the same thickness and surface uniformity as was indicated in the examples above.

During evaluation of the method of the present invention, it was found that the mesh size of the powders used either in the pack or in the alumina barrier dip coat is not critical, the mesh size being varied from about +60 to about -200 without any noticeable difference in effect. The inert barrier, for example of alumina, was found to be useful during processing to control the rate of diffusion and thus to control coating thickness. A shield or shim conforming to the shape of an article or various other means can be used for the same purpose. This barrier was found to be particularly useful in connection with certain nickel base alloys, for example, that of the type shown in Example 2, when used with NaF activator to inhibit any adherence of the pack material to the surface of the article. Such a barrier coating was found generally not to be necessary with the use of NH<sub>4</sub>Cl activator.

The present invention is significantly useful in the protection of articles made from alloys based on iron, nickel or cobalt. However, it can also be very useful in the protection of articles made from materials based on other elements, for example, the refractory metals Cr, Mo, Cb, etc. This can be accomplished by first providing a surface of iron, nickel or cobalt, or its alloys on the article and then co-depositing from a vapor state onto the surface of an alloy of Ti and Al as described above.

#### EXAMPLE 6

A specimen in the shape of a turbine blade made from a chromium base alloy having a nominal composition, by weight, of 7.5% W, 0.2% Ti, 0.8% Zr, 0.1% C, 0.3% Y with the balance Cr was cleaned by first ultrasonic cleaning and then electropolishing in NaOH followed by a dip in a solution of HCl. The specimen was given a nickel strike in a Woods solution and then electroplated with nickel in a sulfamate bath at about 0.8 amp./in.<sup>2</sup> for about 1.5 hours at a temperature of 140° F. After plating, the specimen was placed in the powdered pack mixture described in Example 2 and placed in a retort. The same procedure was followed as in Example 1 except that the temperature within the retort was maintained at 1750° F. for 1 hour. Upon removal, the specimen was found to have an excellent surface treatment and to have the same surface uniformity, lack of substantial change in thickness and excellent oxidation resistance as was indicated in the examples above.

Although the present invention has been described in connection with specific examples and embodiments, it will be understood by those skilled in the arts of metallurgy and surface treatment the various modifications and variations of which the present invention is capable.

What is claimed is:

1. In a method of treating a metallic article surface of a material based on a metal selected from a group consisting of iron, nickel and cobalt, the step of co-depositing titanium and aluminum onto the article surface in a non-oxidizing atmosphere and at a temperature of about 1750-2150° F. from a vapor state of a binary titanium-aluminum alloy consisting essentially of, by weight, more than 15% and less than 50% aluminum, with the balance titanium, in the presence of a halide salt activator selected from the group consisting of NaF, KF and NH<sub>4</sub>Cl.

2. The method of claim 1 in which the binary titanium-aluminum alloy is powdered and consists essentially of, by weight, about 30-35% aluminum, with the balance titanium.

3. The method of claim 2 in which the temperature is about 1750-1975° F. and the halide salt activator is NaF.

4. The method of claim 2 in which the temperature is about 1750–1975° F. and the halide salt activator is  $\text{NH}_4\text{Cl}$ .

5. A method for treating a metallic article surface of a material based on a metal selected from the group consisting of iron, nickel and cobalt, comprising the steps of: cleaning the surface;

immersing the article in a powder mixture consisting of, by weight,

(a) 50–60% alumina;

(b) 38–40% of a powdered binary titanium-aluminum alloy consisting essentially of, by weight, more than 15% and less than 50% aluminum with the balance titanium; and

(c) 0.2–10% of a halide salt activator selected from the group consisting of NaF, KF and  $\text{NH}_4\text{Cl}$ ;

heating the article and powder mixture at a temperature of about 1750–2150° F. in an inert atmosphere for about 1–4 hours to vaporize at least a part of the binary alloy; and then

cooling the article prior to removal from the inert atmosphere.

6. The method of claim 5 in which an inert barrier material is located between the article surface and the powdered mixture and the temperature is from about 1750–1975° F.

7. The method of claim 5 in which the binary titanium alloy in the powder mixture consists essentially of, by weight, 30–35% aluminum, with the balance titanium; the halide salt activator is  $\text{NH}_4\text{Cl}$ ; and the temperature is about 1750–1975° F.

8. The method of claim 6 in which the binary titanium-aluminum alloy in the powder mixture is 30–35% aluminum, with the balance titanium; and the halide salt activator is NaF.

9. The method of claim 5 in which the metallic article surface material is first deposited on an article prior to immersing the article in the powder mixture.

#### References Cited

##### UNITED STATES PATENTS

|           |         |                                 |
|-----------|---------|---------------------------------|
| 1,902,503 | 3/1933  | Howe.                           |
| 2,874,070 | 2/1959  | Galmiche.                       |
| 2,887,420 | 5/1959  | Llewelyn et al. --- 117—107.2 X |
| 3,061,463 | 10/1962 | Samuel ----- 29—196 X           |
| 3,079,276 | 2/1963  | Puyear et al. ----- 117—107.2   |
| 3,096,160 | 7/1963  | Puyear ----- 117—107.2 X        |
| 3,096,205 | 7/1963  | De Guisto ----- 117—107.2       |
| 3,219,474 | 11/1965 | Priceman et al. --- 117—107.2 X |
| 3,262,764 | 7/1966  | Bradley et al. ----- 29—197     |
| 3,263,325 | 8/1966  | Jacobson ----- 117—130 X        |
| 3,061,462 | 10/1962 | Samuel ----- 117—131 X          |
| 3,102,044 | 8/1963  | Joseph ----- 117—131 X          |

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U.S. Cl. X.R.

29—194, 196, 196.2, 197, 198; 117—107.2, 130, 131