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METHOD FOR FORMING AN OXIDATION RESISTANT COATING ON A SUBSTRATE

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This application is a division of application Ser. No. 232,896 filed Oct. 24, 1962, now abandoned.

This invention relates to an oxidation resistant article of a refractory metal or metal alloy and more particularly to an aluminide coating system and method for its application to notch-sensitive refractory metals.

The oxidation resistance of a wide variety of metals and their alloys has been improved through the use of the metal aluminum as a surface coating, usually alloyed with the base metal, at least at the interface between the two. Such a coating may be referred to as an aluminum-base coating or an aluminide coating because of the formation of an aluminide of the base metal, as for example a columbium aluminide. These coatings have been applied in a variety of ways including the application of powdered material and by various molten spray and molten dip techniques, for example as shown in patent application Ser. No. 121,419, Gordon D. Oxx, filed July 3, 1961, now Patent No. 3,186,070, and assigned to the same assignee as the present invention.

It is well known that various alloys of aluminum can be used to provide oxidation resistant coatings on refractory metals, particularly columbium (also known as niobium) and tantalum and alloy systems based on these metals. However, most of the coatings of this type currently known are subject to the handicaps of being quite brittle, causing serious notch embrittlement of the base metal, or both. These effects are especially harmful to the high strength alloys of columbium, many of which are inherently notch sensitive to some extent. A very brittle coating also has the disadvantage of forming a network of fine cracks which allow air to reach the substrate thereby causing contamination and resulting embrittlement of the base metal.

On the other hand, some of the compounds formed between refractory metals and aluminum are highly oxidation resistant and therefore desirable as coatings. For example, three intermetallic compounds can be prepared in the columbium-aluminum system, namely Cb_3Al, Cb_2Al, and $CbAl_3$. Of the columbium aluminides, $CbAl_3$ is the most oxidation resistant as well as the most brittle phase. Corresponding phase relations exist in the tantalum-aluminum system, and the coatings herein described are equally useful on columbium or columbium base alloys and tantalum or tantalum base alloys.

It is an object of this invention to provide an oxidation resistant article of columbium or tantalum or an alloy based on one of these metals having an oxidation resistant aluminum-base coating with minimum susceptibility to crack propagation through the coating or into the base metal.

Another object of this invention is to provide a method for applying an aluminide coating system to columbium or tantalum or an alloy based on one of these metals, the coating system being oxidation resistant and having a barrier which inhibits the propagation of cracks into the base material.

These and other objects and advantages will be recognized from the following detailed description and the examples which are meant to be exemplary of rather than limitations on the scope of this invention.

Briefly, in one form, the present invention provides an article of a refractory metal or alloy having a first coating of silver bonded thereto of a thickness sufficient to cover the entire surface and a second coating of powder metal aluminum-base alloy bonded to said silver coating. The composite body is heat treated to fuse the coatings together and to the base metal.

In another form, the present invention provides an article of columbium or tantalum or an alloy of either, on the surface of which has been fused an aluminide coating in the form of either $CbAl_3$ or $TaAl_3$, which aluminide coating includes silver in solid solution.

In another form, the present invention provides an oxidation resistant article of columbium or tantalum or an alloy of either having an aluminide coating fused to the surface thereof, the coating being predominantly $CbAl_3$ or $TaAl_3$ with silver and another metal, preferably silicon, in solid solution, the coating having a silver and silicon rich portion adjacent the interface between the coating and the base metal. Upon exposure to air at elevated temperatures, an outer skin of Al_2O_3 forms, and an inner layer converts from $CbAl_3$ or $TaAl_3$ to Cb_2Al or Ta_2Al, respectively, with silver and silicon precipitating therefrom. There is some intermixing of these layers.

In another form, the present invention provides a method for coating a notch-sensitive refractory metal alloy with an aluminide coating comprising the steps of applying a silver coating to blanket the surface of the alloy, applying to the silver coated surface an alloy predominately aluminum and then heat treating the coated article to a temperature and for a time sufficient to cause fusion between the aluminum base coating, the silver and the refractory metal.

In each of these embodiments of the invention, an outer coating of aluminum metal may be provided over the aluminum alloy coating.

Wherever Cb_2Al, $CbAl_3$, Ta_2Al or $TaAl_3$ are referred to in this specification, it should be understood that complex aluminides of the form M_2Al and MAl_3 are meant to be included. M is representative of the base metal which can be columbium, a columbium base alloy, tantalum, or a tantalum base alloy. For example, in a columbium base alloy containing 15 percent titanium, M would represent (Cb, Ti) and M_2Al would be $(Cb, Ti)_2Al$. In like manner, when other metals such as, for example, chromium, silicon or titanium are added to the aluminum alloy coating, the coating would contain the complex aluminides of columbium and some or all of the other metals present in either the coating or the base metal alloy.

Suitable materials which may be alloyed with columbium, comprise tungsten, molybdenum, tantalum, zirconium and titanium, this list not being a limitation but given only for purposes of illustrating suitable columbium-base alloys. It is, of course, desirable that the percentage of alloying ingredient in either columbium or tantalum base alloys not exceed an amount which would preclude the proper formation of a protective coating on the body.

Columbium alloys containing amounts of tungsten up to 15 weight percent; molybdenum, 5 weight percent; tantalum, 33 weight percent; titanium, 8 weight percent; and minor amounts of zirconium have been found to be suitable for high temperature use. A columbium alloy with which the present invention is particularly useful is known as F48 and contains nominally about 15 weight percent tungsten, 5 weight percent molybdenum, and 1 weight percent zirconium. Tantalum alloys containing up to 20 weight percent tungsten are also suitable for use with these coatings at elevated temperatures.

Space age requirements have created an increasing demand for oxidation resistant structural materials. Some columbium base alloys such as the type shown in Patent 2,973,261, Frank, assigned to the same assignee as the present invention, show excellent strength properties at 2,500° F. However, their use has been limited by their lack of oxidation resistance. Coating requirements include oxidation resistance, case of application, and prevention of penetration of oxygen and nitrogen, while at the same time the coating must cause minimum reduction in ductility after exposure to air at elevated temperatures. A coating material which appeared to be attractive was aluminum, forming columbium aluminides with the proper heat treatment. Of the columbium aluminides, $CbAl_3$ is the most oxidation resistant but unfortunately is also the most brittle.

It is known that when columbium is given an aluminum base coating in an Ag-Al bath the formation of $CbAl_3$ is suppressed and the only reaction products formed are Cb_2Al and Cb_3Al. One reason for such action is thought to be that the silver diluting the aluminum causes a decrease in the aluminum activity. This type of coating results in a more ductile structure than former aluminide coatings on columbium, but it must be applied by dipping into a molten metal bath.

According to the present invention, the discovery has been made that a coating of silver prior to the application of an aluminum-base slurry coating resulted in the formation of a coating predominantly of highly oxidation resistant $CbAl_3$. In addition, the silver coating provides at the interface either a silver rich barrier to crack propagation or a silver rich, ductile grain boundary layer or a combination of the two. These effects persist after oxidation testing for over ten hours at 2,500° F. in air The silver in this form was unexpectedly found to inhibit the propagation of cracks through the brittle $CbAl_3$ coating matrix and also resulted in an oxidation resistant aluminide coating without causing embrittlement of the base metal. A beneficial effect of the silver plating may be to prevent surface contamination of the base metal by residual oxygen and nitrogen in the argon atmosphere during the fusion treatment and before the outer coatings fuse sufficiently to prevent such contamination.

After a fusion treatment at about 1,900° F. for about one hour in a non-oxidizing atmosphere such as argon, a specimen of F48 columbium alloy that had been silver plated and then slurry coated with an aluminum alloy powder was found to include small entrapped Al_2O_3 particles surrounded by a $CbAl_3$ matrix. X-ray microemission data indicated that silver and silicon (when an aluminum alloy including silicon is used) are uniformly present throughout the coating probably in substitutional solid solution by replacement of aluminum atoms in the $CbAl_3$ phase. After two hours at 2,500° F. in air, the columbium base alloy coated as above was observed to have a first inner portion of substantially all Cb_2Al, an intermediate portion of $CbAl_3$ and an outer portion of Al_2O_3 with some intermixture of the portions. The coating included progressively more columbium toward the columbium alloy-coating interface.

In the following examples, percentages are by weight and mass units are in the avoirdupois system unless stated otherwise.

The preferred method of applying the coating involves three separate layers and can be called a silver and double-slurry coating treatment. The specimens coated in the following examples were carefully cleaned and degreased panels of F48 columbium alloy 1½" x ½" x 0.020" of F48 columbium alloy with well-rounded edges. First, about 0.001 inch of silver is plated on the base metal. This can be done by vapor plating, electroplating, or any other method of applying a coating of silver. This is followed by an aluminum–11% silicon alloy layer and an aluminum overcoat. Both the aluminum alloy and the aluminum are applied in the form of slurries.

One method of silver plating a base metal by means of an electroplating process would begin with careful surface preparation of the base metal by vapor honing and washing in acetone. This is followed by an acid etch for 20 seconds and subsequent rinsing. The silver plating is done with a silver strike for 45 seconds at 5 volts at room temperature followed by a rinse and then plating in a high speed bath for 5 minutes at 5 volts at 100 to 120° F. The silver plated piece is then rinsed and dried. The compositions used in thes steps are as follows:

(A)

Acid etch bath:
Nitric acid, 20 parts.
Hydrofloric acid (48–51%), 20 parts.
Water, 60 parts.

(B)

Silver strike solution:
Silver cyanide, 0.25 oz./gal.
Copper cyanide, 1.50 oz./gal.
Sodium cyanide, 10.00 oz./gal.

(C)

High speed silver plating bath:
Silver cyanide, 14–19 oz./gal.
Potassium cyanide, 15–18 oz./gal.
Potassium carbonate, 2–10 oz./gal.
Potassium hydroxide, 0–4 oz./gal.
Ammonium thiosulphate (60%), 2 fluid oz./100 gal.

The silver plated base metal is then ready for the double-slurry coating. Both of the slurries are prepared by ball milling the mixtures for a period of 2 to 5 hours. The washed, degreased, and dried silver-plated panel is dipped into a slurry of aluminum-11% silicon prealloyed powder using a dip coater at a speed of 8 r.p.m., and the piece to be coated is then removed from the slurry and air dried for 5 minutes. The same process is then repeated with an aluminum powder slurry with the piece subsequently being dried for 8 hours. A typical composition of aluminum-11% silicon slurry follows:

	Grams
Al-11% Si powder —325 mesh	100
Xylene	100
Acryloid (an acrylic resin solution)	50
Bentone 34 (dimethyldioctadecyl ammonium bentonite)	2

The powder used in these slurries is prealloyed, meaning that a homogenous material is formed prior to comminution to powder thereby producing homogeneously alloyed powder particles. The aluminum slurry may be composed of:

	Grams
Reynolds 30LM paste (Al powder —325 mesh)	250
Xylene	150
Acetone	100
Bentone 34	3

An Al-11% Si prealloyed powder is preferred for the first slurry coat because of higher fluidity and better wetting of columbium, tantalum and their alloys. However, chromium, titanium or silicon can be used in varying amounts up to about 50 weight percent but preferably less than about 20 weight percent either as a prealloy or a mixture with the aluminum metal powder, or alternatively, aluminum metal powder can be used without other metals.

The specimens are now ready for heat treatment. They may be suspended from a support beam in an Inconel boat and heat treated inside in an Inconel retort in an electric muffle furnace. After the muffle had been inserted in the retort it is purged with high purity dry argon. The closed retort is then pushed into a preheated furnace. After half an hour at 500° F. when the volatile components in the slurry are driven off, the temperature is raised to 1,900° F. At this temperature all three coated layers are liquid. Surface tension will prevent the liquid

layers from running off, aluminum oxide covering the surface of the powder particles in the slurries and increasing the viscosity. The panels are held in an argon atmosphere until the liquid constituents react and solidify to form a coherent, oxidation-resistant coating. The retort is then pumped down to less than one micron vacuum and maintained at 1,900° F. for another half an hour; however, the entire treatment could be carried out in an inert gas atmosphere. Total time of this fusion treatment is about one hour at 1,900° F.

A preoxidation treatment of exposing a coated and fused article to air at a temperature higher than that of the fusion treatment can be useful for conditioning the coating to provide subsequent protection in air at lower temperatures. This effect results in part from forming a substantial outer layer of Al_2O_3 and in part from some of the innermost $CbAl_3$ converting to the more ductile Cb_2Al with silver and perhaps silicon precipitating from solution in the inner layers. This precipitated silver-silicon phase eventually migrates to the grain boundaries and there causes further ductilization. The preoxidation treatment is optional and would be of benefit primarily when the coated article is to be exposed to an oxidizing atmosphere at relatively low temperatures such as below 2,300° F. Articles to be exposed to air at higher temperatures will undergo this conditioning in use and a separate preoxidation treatment would be of less value for such articles.

It will readily be seen by those skilled in the art that the preoxidation conditioning treatment will be beneficial even if only one of the two preferred conditions is met. An oxidizing treatment without the higher temperature will produce the Al_2O_3 outer layer. A higher temperature than the fusion treatment temperature in a nonoxidizing atmosphere will cause the formation of the Cb_2Al inner layer. However, maximum benefit is obtained from a preoxidation treatment by using a higher temperature than the fusion temperature such as from 2,000° F. to 2,500° F., preferably about 2,300° F., and doing the heating in an oxidizing atmosphere such as air.

Standard oxidation tests of the coated panels were carried out in an electric muffle furnace in static air at 2,500° F. for two hours. Every half hour the samples were taken out of the furnace and inspected for failure. After a 10-hour exposure, the coating showed no sign of edge failure and the bend ductility of the parent or base metal was excellent at room temperature.

Bend tests were performed in a 90° fixture with a 2T radius mandrel on silver-plated and double-slurry coated F48 columbium alloy panels coated as described above. These tests showed a 90° bend angle at room temperature both after the fusion treatment of one hour at 2,500° F. in argon and after subsequent oxidation of 2 hours at 2,500° F. in air.

The coating-base metal system and methods for applying the coatings described in this specification and in the appended claims represent a significant improvement in the art of aluminum-base coatings for columbium and tantalum and alloy systems based on columbium or tantalum. A considerable improvement is found in the ductility properties of bodies coated in accordance with this invention.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The process for forming a protective coating on an exposed surface of a body formed of a base metal selected from the group consisting of columbium, columbium base alloys, tantalum, and tantalum base alloys comprising plating said body with a coating of silver, applying over said silver coating a coating of a metal powder consisting of aluminum and up to 50 total weight percent of at least one metal selected from the group consisting of chromium, silicon and titanium, and fusing said coatings to said base metal by heating said composite body in a non-oxidizing atmosphere at a temperature sufficiently high to cause fusion of the coatings to each other and to the base metal.

2. The process for forming a protective coating on an exposed surface of a body formed of a base metal selected from the group consisting of columbium, columbium base alloys, tantalum, and tantalum base alloys comprising plating said body with a coating of silver, applying over said silver coating a slurry coating of a metal powder consisting of aluminum and up to 50 total weight percent of at least one metal selected from the group consisting of chromium, silicon and titanium, applying over the aluminum base coating a slurry coating of aluminum metal powder to form a composite body, and fusing said coatings to said base metal by heating said composite body in a nonoxidizing atmosphere at a temperature sufficiently high to cause fusion of the coatings to each other and to the base metal.

3. The process of claim 2 wherein the body with the coating fused thereon is heated in an oxidizing atmosphere to a temperature between about 2,000° F. and about 2,500° F.

4. The process of forming a protective coating on an exposed surface of a body of a base metal selected from the group consisting of columbium, columbium base alloys, tantalum and tantalum base alloys comprising electroplating said body with a coating of silver, applying over said silver coating a slurry coating of a prealloyed metal powder consisting of aluminum and up to 20 total weight percent of at least one metal selected from the group consisting of chromium, silicon and titanium, applying over said aluminum coating a slurry of aluminum metal powder to form a composite body, heating said composite body to about 1,900° F. for about one hour in a nonoxidizing atmosphere, and then heating said composite body at about 2,300° F. in an oxidizing atmosphere.

5. The process of claim 4 wherein the prealloyed powder consists essentially of aluminum alloyed with about 11 weight percent silicon.

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