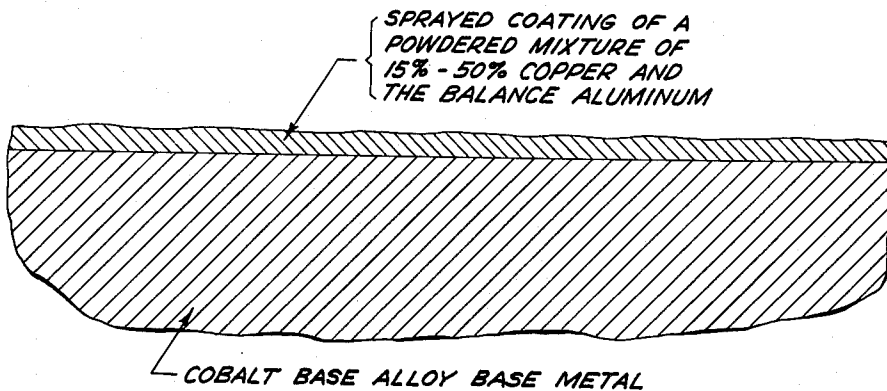


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METHOD OF ALUMINIZING COBALT BASE ALLOYS AND
ARTICLE RESULTING THEREFROM
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METHOD OF ALUMINIZING COBALT BASE ALLOYS AND ARTICLE RESULTING THEREFROM

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This invention relates to the art of providing metals with a heat and corrosion-resistant coating and more particularly to a method of providing cobalt base alloys with a protective coating containing aluminum.

It is well known that an aluminum coating, diffused into the surface of a base metal so as to form an alloy union between the aluminum coating and the base metal, provides the base metal with superior resistance to heat, oxidation, fretting corrosion and other types of corrosion. The commercially successful methods which have been developed for aluminum coating of base metals such as ferrous metals include suitably cleaning the base metal, dipping the base metal in molten aluminum and subsequently heat treating the coated base metal in a molten salt flux to cause a diffusion of the aluminum into the base metal. Another successful method involves applying the aluminum to the base metal in the form of a molten metal spray and thereafter heating the thusly coated base metal in a neutral or reducing atmosphere to effect diffusion of the aluminum into the base metal. Of these methods the latter is particularly desirable since the aluminum coating metal may be efficiently and economically applied by spraying and it lends itself readily to mass production techniques.

Heretofore in so far as it is known, attempts to provide cobalt base alloys with a diffused aluminum coating by a process in which the aluminum is applied by a metal spraying technique followed by a diffusion heat treatment have been unsuccessful for the reason that the aluminum coating did not adhere satisfactorily to the cobalt base metal.

It is a basic object of this invention to provide a cobalt base alloy with a diffused heat, thermal shock and corrosion-resistant aluminum-containing coating in a process in which the aluminum is sprayed onto the cobalt base metal and followed by a diffusion heat treatment. A further object of this invention is to provide high temperature operating articles of manufacture as, for example, ignitor plugs for use in gas turbine engines which are formed of a cobalt base alloy having a heat, thermal shock and corrosion-resistant diffused aluminum-containing alloy at the surface thereof.

These and other objects of the invention are accomplished by first degreasing the cobalt base metal, degassing the metal surfaces and sand blasting the base metal to further clean and roughen the surfaces to be coated, preheating the surfaces to be coated to remove any moisture therefrom, applying a layer of about 0.002 inch to 0.003 inch in thickness to the base metal by flame spraying a mixture of aluminum and copper powder, preferably containing from 20% to 35% copper powder and the balance aluminum powder, and finally subjecting the thusly coated base metal to a diffusion heat treatment at a temperature in the vicinity of about 2100° F. for about one hour or a time sufficient to effect a diffusion of the coating metal into the base metal surface. In the event that the degassing step is omitted, the heat diffusion treatment must be performed in a reducing atmosphere.

Other objects and advantages of the invention will appear from the drawing, the following detailed description of the process of the invention and the coated cobalt base articles resulting from the process.

As is well known, cobalt base alloys have considerable

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utility in high temperature applications such as, for example, in the construction of gas turbine parts such as ignitor plugs and the like. An example of a preferred cobalt base alloy to which the present invention relates has the following composition:

	Percent
Carbon	0.05 to 0.15.
Chromium	19 to 21.
Nickel	9 to 11.
Tungsten	14 to 16.
Silicon	Up to 1.
Manganese	1 to 2.
Iron	Up to 3.
Cobalt	Balance.

Examples of other cobalt base alloys illustrating the type of alloys involved in the present invention are as follows:

Alloy A

	Percent
Carbon	0.25
Silicon	0.6
Manganese	0.6
Chromium	27.0
Nickel	3.0
Cobalt	62.0
Molybdenum	5.0
Iron	1.0

Alloy B

	Percent
Carbon	0.4
Silicon	0.6
Manganese	0.3
Chromium	24.0
Nickel	2.0
Cobalt	66.0
Iron	1.0
Tungsten	6.0

Alloy C

	Percent
Carbon	0.4
Silicon	0.6
Manganese	0.3
Chromium	25.0
Nickel	32.0
Cobalt	34.0
Molybdenum	6.0
Iron	1.0

Alloy D

	Percent
Carbon	0.4
Silicon	0.6
Manganese	0.6
Chromium	24.0
Nickel	16.0
Cobalt	51.0
Molybdenum	6.0
Iron	1.0

Alloy E

	Percent
Carbon	0.4
Silicon	0.6
Manganese	0.6
Chromium	25.0
Nickel	10.0
Cobalt	55.0
Iron	1.0
Tungsten	8.0

In a specific embodiment of this invention, a specimen in the form of an ignitor plug casing is formed of a co-

balt base alloy consisting of about 0.10% carbon, 20% chromium, 10% nickel, 15% tungsten, 1% silicon, 1.5% manganese, 2% iron and the balance cobalt. The cobalt base alloy specimen is first degreased and cleaned in any suitable manner well known in the art. Next the specimen is subjected to heat at a temperature of about 1650° F. for about one hour while maintaining it under a vacuum of about 0.1 inch of mercury pressure to eliminate the gases such as oxygen, nitrogen and the like from the surface of the alloy specimen and then is cooled under vacuum. This is performed by inserting the specimen in a ferrous metal container, evacuating the container and then inserting it in a furnace maintained at about 1650° F. After the heat treatment, the container is removed and permitted to cool so that the specimen is cooled under the vacuum conditions. This is an important step of the process since it results in a markedly improved diffusion bond of the coating metal to the specimen base metal in the steps hereinafter described and is essential unless the diffusion heat treatment is performed in a reducing atmosphere. The specimen is then sand blasted to clean and roughen the metal surfaces and to remove a dark film which forms on the metal surface as a consequence of the degassing heat treatment.

The specimen is given a degassing heat treatment under vacuum and for a time and at a temperature to eliminate the entrapped gases contained in the base metal surfaces to at least the depth to which it is expected the subsequently applied coating will diffuse. Thus, a degassing heat treatment under vacuum at 1650° F. for about one hour will remove gases to a depth of about 0.0035 inch which is sufficient for most applications of the present invention. The heat treatment described may be performed at temperatures ranging from about 1000° F. to about 2400° F. or a temperature below the softening temperature of the base metal for a time sufficient to effect the degassing to the desired depth. The rate of degassing is a function of both time and temperature and the particular degassing condition to be employed is largely a matter of choice.

A powdered metal mixture is prepared which consists of 30% by weight of an unoxidized copper powder of a particle size such as to pass a 325 mesh screen thoroughly admixed with 70% by weight of an atomized aluminum powder of a particle size such that 100% thereof would pass a 100 mesh screen and 80% thereof would pass a 325 mesh screen. After thoroughly mixing the powders, the powder mixture is dried for about one hour at about 200° F. to remove any moisture adhering to the powder.

Next, utilizing a Wall-colomonoy powder spray gun and adjusting the fuel valves so as to maintain a neutral spray gun flame, the ignitor plug specimen is preheated with the gun flame to a temperature of about 200° F. to volatilize any moisture on the surface of the specimen. The use of a neutral flame for preheating the specimen produces improved results in the protective coating. Other powder flame spray guns may, of course, be used. Care must be taken to avoid heating the specimen to temperatures at which oxides may form on the specimen surface. Preheating temperatures of from 175° F. to 225° F. are satisfactory. Meanwhile, care is exercised to insure that the specimen is not contaminated after the sand blasting and degassing procedure. After preheating the specimen, the powder supply for the spray gun is turned on and a coating of the metal of about 0.0035 inch in thickness is applied as shown in the drawing. A sprayed thickness of metal of about 0.002 inch is essential to provide a satisfactory coating. A layer in excess of 0.0035 inch may be applied without adverse results. However, since the sprayed metal in excess of 0.0035 inch will not appreciably increase the thickness of the final diffused case or coating, no appreciable benefit is gained from the application of a coating layer in excess of 0.0035 inch in thickness. Extending the heat diffusion treatment at

2100° F. to a period of about 15 hours increased the total case thickness only about 0.005 inch.

Thereafter, the coated specimen is placed in a furnace maintained at about 2100° F. for about one hour. The diffusion heat treatment is conducted for a period of time sufficient to develop a case or diffused coating layer of from 0.002 inch to 0.0035 inch. Furnace temperatures of from 2000° F. to 2250° F. may be employed with satisfactory results. The rate of diffusion is a function of both time and temperature so that a diffusion temperature of about 2000° F. requires a time period of about two hours, whereas a diffusion of 2250° F. requires a time period of about ½ hour to develop a satisfactory case thickness. Diffusion temperatures in excess of 2250° F. are undesirable because of adverse effects on the structure whereas diffusion temperatures below 2000° F. require an excessive diffusion time period. If the aforementioned degassing step is omitted, it is essential that the heat treatment be performed in a reducing atmosphere. To this end, an atmosphere of hydrogen or disassociated ammonia is maintained in the furnace. The specimen is then cooled at room temperature under reducing atmospheric conditions. After the cooling operation, the specimen is preferably blasted with a fine alumina powder to a satin finish.

A micrographic examination of the specimen disclosed a case or coating formed of two distinct layers. The outer layer had a thickness of about 0.0015 inch, a columnar structure, and consisted essentially of an aluminum low copper content alloy. The inner layer had a thickness of about 0.0017 inch and consisted of a complex intermetallic alloy of aluminum, copper and elements from the base metal. At the interface of the two layers, but included in the inner layer, was a copper segregation. The precise metallurgical composition of these case layers is not at present completely known, and accordingly it is not intended that the invention be limited to the particular composition observed and set forth above. The Rockwell "C" hardness of the inner layer was about 60.0 and the Rockwell "C" hardness of the outer layer was about 59.0. The Rockwell "C" hardness of the base metal was about 26.0.

The specimen was found to pass the adherence and corrosion resistance requirements including fretting corrosion resistance for its use as an ignitor casing for use in gas turbine engines. Specifically, the adherence and corrosion properties were tested by a six cycle exfoliation test of which each cycle consisted of heating the specimen for 10 minutes at about 1850° F. followed by a water quench. No scaling or oxidation was observed or no chilling or lifting of the coating was observed after the six cycles of the test. The specimens were subjected to cutting with a rubber wheel to determine the ductility of the case. No chipping was observed.

A series of test specimens were made using coating powders ranging from 5% to 50% copper and the balance aluminum powder. Optimum fretting corrosion resistance was obtained using coating powder mixtures ranging from 25% to 30% copper powder and the balance aluminum powder. Desirable adherent, hard, corrosion-resistant coatings were obtained using powder mixtures using powders ranging from 20% to 35% copper and the balance aluminum. These coatings involved inner case layers ranging from about 0.0007 inch in thickness to about 0.0016 inch and a total case thickness ranging from about 0.002 inch to about 0.0035 inch. Specimens formed using these powder mixtures had an inner layer case Rockwell "C" hardness of about 41 to 60.0 and an outer layer case Rockwell "C" hardness of about 35 to 59. The Rockwell "C" hardness of the base metal in contrast ranged from about 26 to 32. Specimens prepared utilizing a powder mixture containing less than 15% copper produced an outer case layer which was excessively brittle. On the other hand, specimens utilizing powdered coating containing an excess of 50%

copper had an excessively soft outer case layer. Useful adherent coatings for various purposes may be formed of powders ranging from 15% to 50% copper and the balance aluminum.

Desirable coatings involve a total case consisting of outer and inner layers ranging from 0.002 inch to 0.0035 inch. A satisfactory case is obtained when the inner layer is in the range of 0.0007 inch to 0.0012 inch.

As above-indicated, the interpenetration of the coating metal and the base metal atoms during the heat treating period forms a complex inner alloy layer which must possess a tight adherence and high hardness without brittleness. These qualities improve the resistance to elevated temperatures and fretting corrosion. The specimens coated as indicated above were provided with a hard, adhering, heat-resistant coating which is markedly superior to that of the base metal. The coatings further provide the specimens with improved thermal shock resistance, burn resistance and improved resistance to carbonaceous deposit formation.

While the invention has been described by means of certain specific examples, it is to be understood that the scope of the invention is not to be limited thereby except as defined in the following claims.

I claim:

1. A method of providing a cobalt base alloy with an adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising flame spraying a powdered mixture consisting substantially of 15% to 50% by weight copper and the balance aluminum onto said surface to form a coating of at least about 0.002 inch in thickness and thereafter subjecting the coated base metal to a heat treatment to cause a diffusion of said coating into the base metal.

2. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising flame spraying a powdered mixture consisting of about 20% to 35% by weight copper and the balance aluminum onto said alloy surface to form initially a coating of at least about 0.002 inch in thickness and thereafter subjecting the coated alloy to a heat treatment ranging from about 2000° F. to 2250° F. and for a time sufficient to effect a diffusion of the coating into the base metal.

3. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising flame spraying a powdered mixture consisting of about 25% to 30% by weight copper and the balance aluminum onto said surface to form initially a coating of at least about 0.002 inch in thickness and thereafter subjecting the coated alloy to a heat treatment ranging from about 2000° F. to 2250° F. and for a time sufficient to effect a diffusion of the coating into the base metal.

4. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising cleaning said surface to be coated and removing the moisture therefrom, degassing said alloy surface, flame spraying a powdered mixture consisting of about 20% to 35% by weight copper and the balance aluminum onto said surface to form a coating thereon of at least about 0.002 inch and thereafter subjecting the coated alloy to heat at a temperature of from about 2000° F. to 2250° F. for a time sufficient to cause a diffusion of the coating into the base metal.

5. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising cleaning said surface and removing the moisture therefrom, flame spraying a layer of at least 0.002 inch of a powder consisting of from about 20% to 35% by weight copper and the balance aluminum and thereafter subjecting the coated alloy to heat at a temperature of from about 2000° F. to 2250° F. while surrounded by a reducing atmosphere for

a time sufficient to cause a diffusion of the coating metal into the base metal surface.

6. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising degassing said surface by subjecting it to heat while under a vacuum at a temperature and for a time sufficient to degas the base metal surface to between 0.002 inch and 0.0035 inch, cooling said surface while under a vacuum, cleaning said surface and removing the moisture therefrom, flame spraying a layer of at least 0.002 inch of a powder consisting of about 20% to 35% by weight copper and the balance aluminum, and thereafter subjecting the coated metal surface to a heat treatment of between 2000° F. and 2250° F. for a time sufficient to form a diffused coating of at least about 0.002 inch in thickness.

7. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on a surface thereof, the steps comprising degassing said surface by subjecting it to heat while under a vacuum at a temperature and for a time sufficient to degas the base metal surface to between 0.002 inch and 0.0035 inch, cooling said surface while under a vacuum, cleaning and roughening said surface, preheating the base metal by means of a neutral flame to drive moisture therefrom, flame spraying a layer of at least 0.002 inch of a powder consisting of about 25% to 30% by weight copper and the balance aluminum, and thereafter subjecting the coated metal surface to a heat treatment of between 2000° F. and 2250° F. for a time sufficient to form a diffused coating of at least about 0.002 inch in thickness.

8. A method of providing a cobalt base alloy with a tightly adherent heat and corrosion-resistant coating on the surface thereof, the steps comprising degassing said surface by subjecting it to heat while under a vacuum at a temperature and for a time sufficient to degas said surface to between 0.002 inch and 0.0035 inch, cooling said surface while under a vacuum, cleaning and roughening said surface, preheating said surface by means of a neutral flame to remove the moisture therefrom, flame spraying a layer of from 0.002 inch to 0.0035 inch of a powder consisting of about 20% to 35% by weight copper and the balance aluminum, and thereafter subjecting the coated metal surface to a heat treatment of between about 2000° F. to 2250° F. for a time sufficient to form a diffused coating of from 0.002 inch to 0.0035 inch in thickness comprising an inner layer including a complex intermetallic alloy of alumina, copper and elements of the cobalt base alloy and having a thickness of between about 0.0007 inch to 0.0012 inch and an outer layer consisting of an aluminum-copper alloy.

9. A cobalt base alloy having a tightly adherent heat and corrosion-resistant coating on a surface thereof, said coating consisting of a diffusion layer of at least about 0.002 inch in thickness formed by diffusing a mixture of copper and aluminum powders consisting of from about 20% to 35% by weight copper and the balance aluminum.

10. A cobalt base alloy having a tightly adherent heat and corrosion-resistant coating on a surface thereof, said coating consisting of a diffusion layer of from about 0.002 inch to 0.0035 inch in thickness formed by diffusing a mixture of powders consisting of about 20% to 35% by weight copper and the balance aluminum.

11. A cobalt base alloy comprising by weight about 0.05% to 0.15% carbon, 19% to 21% chromium, 9% to 11% nickel, 14% to 16% tungsten, silicon up to 1%, 1% to 2% manganese, up to 3% iron and the balance cobalt, and having a tightly adherent heat and corrosion resistant coating formed thereon, said coating consisting of a diffusion layer having a thickness of about 0.002 inch to 0.0035 inch and being formed by diffusing a powdered mixture consisting of about 20% to 35% by weight copper and the balance aluminum.

12. An ignitor plug casing or the like for use in connection with gas turbines or the like comprising a cobalt base alloy comprising by weight about 0.05% to 0.15% carbon, 19% to 21% chromium, 9% to 11% nickel, 14% to 16% tungsten, silicon up to 1%, 1% to 2% manganese, up to 3% iron and the balance cobalt, and having a tightly adherent heat and corrosion-resistant coating thereon, said coating consisting of a diffusion layer having a thickness of about 0.002 inch to about 0.0035 inch formed by diffusing a powdered metal mix-

ture consisting of about 20% to 35% by weight copper and the balance aluminum.

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