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COATINGS FOR COLUMBIUM BASE ALLOYS

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This invention relates to novel coatings for columbium and columbium base alloys that will protect the base metal or alloy from oxidation in very high temperature environments and to a method for creating such coatings. More particularly, this invention relates to coatings produced by vapor deposition or by electrodeposition and diffusion of cobalt aluminide (CoAl) over columbium or columbium base alloys and to a method for achieving vapor deposition and electrodeposition of CoAl on these columbium base materials to produce a protective coating of the compound CoAl over the base metal that provides an oxidation resistant coating at very high temperatures, such as, for example, temperatures up to at least 2500° F.

The principal limitation in gas turbine technology today is the maximum turbine inlet temperature. The turbine inlet temperature is, in turn, set by the temperature that the turbine vanes and blades are able to withstand without danger of failure. Formerly, the best available high temperature alloys were nickel and cobalt base superalloys, but critical structural components, such as turbine vanes and blades constructed from such alloys, are limited to maximum operating temperatures of between 1600° and 1900° F.

For many years it has been generally known that the high temperature strength properties of metals are closely related to their melting points. Thus, metals having high melting points also tend to have high temperature strength potentials.

The need for structural materials for service at temperatures in excess of those obtainable with existing materials of construction, such as, nickel and cobalt alloys, has stimulated interest in the metals having the highest melting points, or the refractory metals, particularly, chromium, columbium, molybdenum, and tungsten. Until recently molybdenum was considered the chief prospect for such usage. However, at the high temperature service conditions needed, molybdenum oxidizes at a catastrophic rate, principally because molybdenum oxide is volatile at elevated temperatures.

As an alloy base material for high temperature service, columbium offers promise, and considerable interest has been directed to its use as a structural alloy base for applications in high-temperature environments. Among the technically most important physical qualities of columbium as an alloy base are its high melting temperature (4380° F.) and its low neutron-capture cross-section. Columbium is, therefore, potentially useful for such applications as fast aircraft, space flight vehicles, and nuclear reactors.

Further, columbium is inherently a soft, ductile, readily formable material. Although its melting temperature is about 4380° F., pure columbium becomes too weak for practical structural uses at temperatures above 1200° F. Columbium is also a very reactive metal in that it dissolves large quantities of oxygen and probably nitrogen, on exposure to atmospheres containing even small amounts of these elements at modest temperatures.

The history of columbium alloy technology has demonstrated the incompatibility of achieving oxidation resistance and high-temperature strength through alloying alone. Since the major fields of utility for columbium base alloys depend largely upon retention of high-tempera-

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ture strength in the alloys, it is apparent that useful classes of columbium alloys will demand coatings for protection when used in their normal high temperature oxidizing environments.

Coatings of typical classes used for columbium base substrates are hard and brittle and are thus subject to cracking or other failure at localized sites. In contrast to molybdenum which oxidizes catastrophically, the oxide of columbium does not volatilize, and it is thus potentially possible to prevent oxygen attack on columbium by coating the metal, and should premature localized coating failure occur, to restrict the failure and oxygen attack to the localized site. Further advantages offered by columbium base alloys over molybdenum base alloys are that columbium base alloys are relatively more ductile and workable at low temperatures and columbium has a lower density than molybdenum.

A particularly important potential area of use for columbium base alloys as dictated by economic and technological considerations is in applications of such alloys requiring exposure to oxidizing environments at temperatures up to about 2500° F. (a temperature that clearly establishes utility for columbium base alloys), with the concomitant requirement that the alloys must be able to resist strong stresses for appreciable periods of time at such high temperatures. About 1000° F. is the maximum temperature to which high stress-rupture strength columbium alloys may be subjected for extended times in the uncoated condition without serious oxidation, and at temperatures above 1000° F. the oxidation problem becomes acute.

The art has previously recognized oxidation resistant intermetallic coatings that exhibit particular potential for protecting refractory metals (e.g., columbium, molybdenum, tantalum, and tungsten) from oxidation at high temperatures. In general, the more effective of these intermetallic coatings are further classified as silicides, aluminides, and beryllides of the base metal. In considering coatings for the refractory metals, both coating and substrate materials are important to the performance of the coated systems. For example, silicide coatings over columbium and molybdenum may perform very differently, with the difference in performance attributable to the substrate rather than the coating type. As an additional confirmation of the importance of the substrate, some species of coatings that are reliably protective over, for example, tantalum are ineffective over columbium, because they are susceptible to premature localized defect failures at high temperatures.

Several methods, such as, flame or plasma torch spraying, slurry application techniques, electrophoretic deposition, hot pressure bonding or vapor deposition, may be used for applying intermetallic coatings to columbium base alloys. A vapor deposition process that can be employed advantageously with some types of coatings is the so-called pack-cementation process, in which the object to be coated is surrounded by a particulate pack mixture containing, for example, the metal to be reacted with or deposited upon the object to be coated (e.g., silicon, aluminum, beryllium), an activator or energizer (usually a halide salt, such as, NaCl, KF, NH₄I, NH₄Cl, and the like), and an inert filler material (e.g., Al₂O₃, SiO₂, BeO, MgO, and the like). This mixture, held in a suitable container (steel box, graphite boat, or refractory oxide crucible, for example), is then heated to a desired coating temperature in a prescribed atmosphere and held for a length of time sufficient to achieve the desired coating. When conducted properly, the pack-cementation process will result in controlled-thickness coatings on, for example, columbium, the major proportions of which will be, for example, CbAl₃ or CbSi₂, and the like.

The more favorable coatings for columbium (columbium aluminides, silicides, beryllides) possess certain intrinsic deficiencies, such as rapid oxidation failure at low temperatures (in the vicinity of 1300° F.) or at high temperatures (greater than about 2000° F.). Perhaps, the most serious deficiency of existing coatings for columbium, however, is their propensity for failure at localized sites. Research has shown that two properties contribute greatly to this propensity for localized failure in existing coatings:

(1) The extreme brittleness of existing coating materials; and

(2) Thermal expansion mismatch between coating and substrate.

Copending application Serial No. 65,962, filed October 31, 1960, discloses and claims a class of fabricable, ductile, stress-rupture resistant columbium base alloys that will readily fulfill the structural requirements for use at high temperatures up to at least about 2500° F. Typical of this latter class of alloys is the composition Cb-20Ta-15W-5Mo (additions expressed in percent by weight).

In view of the foregoing, it is a primary object of this invention to provide a coating composition that will protect such stress-rupture resistant alloys from the effects of oxidation at temperatures up to about 2500° F., and that in spite of a thermal expansion mismatch between the coating and columbium base alloys, will nevertheless achieve a ductile coating for such alloys that is highly resistant to failure at localized sites.

Additional objects of this invention are to provide a coating and a method for coating columbium and columbium base alloys: (1) that achieves a coating which, in addition to protecting the alloys from oxidation at high temperatures, is also capable of withstanding severe mechanical and thermal stresses, such as are encountered in jet engine service; (2) that is compatible with the base material of the alloy, so that the coating will not form low-melting phases or phase mixtures, volatile compounds, or a thick brittle layer; and (3) that has mechanical properties that are reasonably matched to the base metal or substrate.

Further objects of this invention are to provide a coating for columbium and columbium base alloys that will have as intrinsic characteristics: superior oxidation resistance and thermal stability over a temperature range up to about 2500° F.; adequate diffusional stability (i.e., the coating method provides some initial diffusion between the coating and the substrate but the resultant coating exhibits stability at operating temperatures to both oxidation and further diffusion); superior ductility at elevated temperatures; and creation of an inherent continuous coating both during initial application and during use at operating temperatures.

Other objects of this invention are to provide a coating for columbium and columbium base alloys: that in thicknesses of about 2 mils or more will be capable of providing for exposures to high temperature oxidizing environments for times in excess of 100 hours at 2200° F.; that despite a relatively high level of thermal expansion mismatch between the coating and columbium alloys, achieves a significantly higher resistance to cyclic fatigue failure than has been achieved by previously existing less ductile diffusion coatings, such as, columbium aluminide (CbAl₃); that is not sensitized toward rapid low temperature oxidation failure at temperatures, such as, 1300° F., by prior extended exposures at higher temperatures, such as, 2200° F., thereby exhibiting very high thermal stability of oxidation properties; and that will tolerate substantial contamination with foreign ingredients or phases without seriously impairing its protective capability.

Still further objects of this invention are to provide a method for depositing such coatings on columbium and columbium base alloys that includes as preferred processes: (1) vapor deposition by a two-cycle pack-cementa-

tion process; (2) electrodeposition (more specifically, electroplate-diffusion process); and (3) a combined two-step electrodeposition and vapor deposition process. These various methods of depositing the coatings of this invention achieve substantial uniformity and continuity in the coating and yield an essentially uniform and continuous coating on even intricately shaped parts and at the edges and corners of parts to provide an oxidation resistant coated metal body having a columbium base core or substrate.

Additional objects and advantages of the invention will be set forth in part in the description that follows, and in part will be obvious from the description, or may be learned by practice of the invention, the objects and advantages being realized and attained by means of the compositions, methods, and processes particularly pointed out in the appended claims.

To achieve the foregoing objects, and in accordance with its purpose, this invention, in one of its forms, provides a new and improved coating for columbium and columbium base alloys comprising a high-temperature, ductile, oxidation resistant, diffusional stable, cyclic fatigue failure resistant metal alloy consisting, apart from impurities, of CoAl. The new and useful result of the invention may also be achieved with CoAl that also contains a dissolved metal, the dissolved metal being a metal selected from the group consisting of cobalt in an amount of up to 30 atomic percent in excess of the stoichiometric quantity of cobalt in the CoAl (50 atomic percent) and aluminum in an amount up to about 2 atomic percent in excess of the stoichiometric quantity of aluminum in the CoAl (50 atomic percent).

In another embodiment, this invention, embraces an article of manufacture having good stress-rupture strength at high temperatures, high-temperature oxidation resistance, and resistance to cyclic fatigue failure, which comprises a core of metal selected from the group consisting of columbium and alloys thereof, the article having a surface layer consisting essentially of CoAl. In a slightly modified form of the latter embodiment, the article may have a surface layer consisting essentially of CoAl and a sublayer consisting essentially of associated cobalt and columbium containing material, the sublayer being between the surface layer and the core.

In accordance with its purpose, this invention includes a method of producing a coated metal article having resistance to oxidation at high temperatures and good stress-rupture strength at high temperatures, which method comprises depositing a surface coating of CoAl on a metal substrate selected from the group consisting of columbium and alloys thereof. One embodiment of such method includes a two-cycle vapor deposition process which comprises first cobaltizing the metal substrate by vapor depositing cobalt thereon and then aluminizing such cobaltized metal substrate by vapor depositing aluminum thereon to create a coating on the metal substrate consisting essentially of the compound CoAl, or the compound CoAl together with a sublayer consisting essentially of associated cobalt and columbium containing material.

In another form, such method comprises placing a thin deposit of cobalt on the metal substrate by a suitable technique, such as vapor deposition, flame or plasma torch spraying slurry application, hot pressure bonding, or the like, to form a very thin substantially continuous layer of cobalt over the substrate surface. The metal body with this thin coating of cobalt is then exposed as a cathode in a cobalt containing electroplating bath to produce a cobalt electrodeposit of a desired thickness on the substrate. Further steps in this method include exposing the cobaltized substrate as a cathode in an electroplating bath containing aluminum to produce a coating of aluminum on the cobaltized substrate and then heat treating the substrate at temperatures up to about 2200° F. to form CoAl as a surface layer on the substrate.

It is impossible to electrodeposit cobalt on a columbium base substrate by conventional electrodeposition methods. It has been found, however, that if a thin coating of cobalt is first placed on the substrate by some efficacious method, preferably by vapor deposition using a pack-cementation process, the electrodeposited cobalt can then be made to adhere satisfactorily to the existing thin cobaltized surface of the substrate and a successful electrodeposition of cobalt can be achieved, even though cobalt can not be electrodeposited on a plain columbium base substrate by any known methods.

When an electrodeposition method is used with this invention, the columbium base substrate may also be prepared to receive electrodeposited cobalt by electroplating a thin iron strike from a bath containing iron on the substrate. The ferritized substrate should be outgassed in a vacuum for a substantial period of time (e.g., about 20 hours) at a raised temperature (e.g., about 400° F.), and then diffused in a vacuum at a high temperature, (e.g., about 1 hour at about 1300° F.). It has been found that the thin iron strike on the substrate surface successfully promotes adherence of cobalt from a cobalt electroplating bath.

In a still further and preferred embodiment, the method comprises exposing the substrate as a cathode in a cobalt containing electroplating bath, after preparation of the substrate surface by a thin deposit of cobalt or iron as described above, to produce a cobalt electrodeposit on the substrate, enclosing the cobaltized substrate in an aluminizing pack of powdered material containing a source of aluminum and a small amount of a volatilizable halogen generating substance as essential active ingredients and an inert filler, and heating the article in the pack to a temperature higher than that causing volatilization of the halogen substance to effect the creation of an exterior surface layer composed predominantly of CoAl as an alloy or intermetallic compound on the substrate. This latter method is particularly efficacious in producing a desirable substantially uniform and continuous coating of CoAl over the substrate.

As previously stated, the most serious deficiency of existing coatings for columbium is their propensity for failure at localized sites. Two of the properties of existing coatings that contribute greatly to this propensity toward localized failure are:

- (1) Their extreme brittleness, and
- (2) Thermal expansion mismatch between the coatings and columbium base substrates.

Quite surprisingly, however, with the coatings of this invention, even though a high degree of thermal expansion mismatch exists between the coatings and the substrate, the coatings have such a high degree of ductility and other desirable properties that they function adequately and avoid any particular propensity toward localized failure.

Certain oxidation resistant intermetallic compound types of material exhibit relatively broad solubilities for their constituent elements. It has been shown that materials of this class normally display superior ductilities to the "line" compounds, that exhibit little solubility for their constituent elements. This invention is directed to cobalt aluminide (CoAl) as a coating for columbium base alloys, and CoAl is a compound of the former type, i.e., it exhibits relatively broad solubilities for its constituent elements. In accordance with this invention, CoAl, in addition to its ductility potential, displays good oxidation resistance at high temperatures and a high melting temperature, both of which properties make it an attractive coating for columbium base materials.

Although it is preferred that stoichiometry be achieved with the CoAl coating compound of this invention, and although stoichiometry calls for 50 atomic percent cobalt and 50 atomic percent aluminum in the composition of the coating, the new and useful result of the invention may also be achieved with a CoAl composition in which

cobalt is dissolved in excess of the stoichiometric quantity by up to about 30 atomic percent or in which aluminum is dissolved in excess of the stoichiometric quantity by up to about 2 atomic percent.

Further, in accordance with this invention, CoAl is superior to such compounds as, for example, CbSi₂, CbAl₃, and several of their modifications, as a coating material for columbium base alloys that will protect the substrates from oxidation during elevated temperature exposures.

To demonstrate the effectiveness of CoAl as a coating material for columbium base alloys, and in accordance with this invention, CoAl compound was prepared in massive form by tungsten-electrode-arc-melting a charge consisting of 68 percent by weight of cobalt and 32 percent by weight of aluminum under a partial pressure of high purity helium. The homogenized melt was cast to form a ½-inch diameter by 4-inch long rod. This rod was then machined to further prepare specimens as required for oxidation, thermal expansion and diffusion testing.

Oxidation tests were conducted in air at temperatures of 1000°, 1300°, 1600°, 1900°, 2200°, and 2500° F. for total times of 100 hours. During these tests, the specimens were generally cooled to room temperatures at 25 hour intervals for weighing and visual examination. Temperature, ° F.: mg./cm.²/100 hr. tion resistance, as indicated by the following cumulative 100-hour weight gains set forth in Table 1:

Table 1

Temperature, ° F.:	Cumulative weight gain, mg./cm. ² /100 hr.
1000	0.0
1300	0.1
1600	0.5
1900	0.5
2200	2.9
2500	4.7

¹ Estimated.

By comparison, aluminide reaction coating materials for columbium and its alloys formed by reaction with the substrate [i.e., the MAI₃ type, where M represents the proportionate ingredients of the substrate (and is so used throughout this document), such as CbAl₃ or (Cb-20Ta-15W-5Mo)Al₃]

exhibit poor oxidation resistance, as shown in Table 2 below:

Table 2

Coating Material	Test Temperature, ° F.	Time, hr.	Cumulative Weight Gain, mg./cm. ²
CbAl ₃	1,000	75	48
CbAl ₃	1,300	25	213
CbAl ₃	1,600	50	30
CbAl ₃	1,900	100	16
CbAl ₃	2,200	100	81
(Cb-20Ta-15W-5Mo)Al ₃	1,300	25	66
(Cb-20Ta-15W-5Mo)Al ₃	2,200	25	336

In accordance with the invention, the resistance of CoAl to deterioration during cyclic oxidation is thus vastly superior to that of the normal columbium base alloy trialuminides.

An additional oxidation test was performed on the CoAl specimen that had been oxidized for 100 hours at 2200° F. This specimen was furnace-cooled from 2200° F. to room temperature without deterioration, and subsequently oxidized for 100 hours at 1300° F. without any significant deterioration, thus displaying the excellent thermal stability of oxidation properties of the coating material of this invention. Even when, by propitious modification, trialuminide coatings for columbium and its alloys are made to display attractive oxidation resistance over the temperature range from 1000° to 2500° F., such

coatings may be sensitized toward rapid low temperature failure at 1300° F. prior extended oxidation at 2200° F.

A diffusion couple consisting of CoAl metallurgically bonded to a representative columbium base alloy, Cb-20Ta-15W-5Mo, was annealed for 100 hours at 2200° F., and the couple displayed very little depletion of the CoAl coating at this elevated temperature. Metallographic examination of this treated couple showed a uniform diffusion zone 1-mil thick to exist after the 100 hour, 2200° F. treatment. Microhardness traverses showed the total width of the diffusion zone was 1.5 mils, which included slight additional solution effects not apparent visibly. Thus, the diffusional stability between CoAl as a coating and Cb-20Ta-15W-5Mo, representative of structural alloy substrates, was more than adequate for the new and useful result taught by this invention. Thermal expansion of CoAl was measured in a recording dilatometer at temperatures from room temperature through 2500° F. The results, as well as expansion data for columbium and one of its representative alloys, are given in Table 3 below:

Table 3

Material	Mean Linear Thermal Expansion Coefficients from 68° F. to Indicated Temperatures, in./in./° F./10 ⁶				
	500	1,000	1,500	2,000	2,500
CoAl.....	6.4	7.1	7.7	8.4	9.5
Cb.....	4.0	4.2	4.4	4.6	4.7
Cb-20Ta-15W-5Mo.....	3.7	3.9	4.1	4.3	4.5

In accordance with the invention, the high temperature ductility of CoAl is so superior that it unexpectedly counteracts the poor thermal expansion match displayed between CoAl and columbium base materials.

In the examples of the use of the coatings of this invention, two different substrates were used. These substrates were:

- (1) Unalloyed columbium, ¼-inch rod; and
- (2) An alloy of Cb-20Ta-15W-5Mo (additions in percent by weight), representative of columbium base alloys and hereafter referred to as "the Alloy," ½ to ¼-inch diameter rod.

The CoAl coatings of this invention are equally operable with columbium base alloys other than the particular alloy selected to exemplify the new and useful result of the invention, and it will be understood by those skilled in the art that the CoAl coatings of this invention may be deposited on any useful columbium base alloy to achieve the desired results of the invention. Further, in addition to the specific methods described herein as exemplifying processes by which CoAl coatings of this invention may be deposited upon substrates of columbium and its alloys, other methods, such as flame or plasma torch spraying, slurry application techniques, electrophoretic deposition or hot pressure bonding, and the like are also efficacious in producing the new and desirable coatings of this invention.

In accordance with the invention, CoAl coatings may be applied to such substrates by using a two-cycle pack-cementation process, in which the first cycle comprises embedding chemically cleaned and polished specimens to be coated in a cobaltizing pack mixture; the following mixture is typical:

15 percent by weight of cobalt powder;
3 percent by weight of NH₄Cl powder;
82 percent by weight of Al₂O₃ powder.

The desired results of this invention can be achieved by cobaltizing in packs containing from about 10 to 40 percent by weight of cobalt, preferably from 15 to 30 percent by weight of cobalt, and from about 2 to 12 percent by weight of NH₄Cl, preferably from about 3 to 9 percent by weight of NH₄Cl, balance an inert filler mate-

rial, such as, Al₂O₃ powder. The packs, contained in covered steel cans or graphite cups, may then be subjected to various thermal treatments in an argon atmosphere at temperatures ranging from about 1400° to 2200° F. for times from about 4 to 8 hours, as required to deposit a desired amount of cobalt.

During this treatment, cobalt reacts with the substrate to form, for example, the compounds M₃Co and M₂Co₃, or other cobalt-rich layers at the surface, where M represents about the proportionate ingredients as they occur in the substrate. For example, cobalt-rich coatings over columbium will be found to contain the compounds Cb₃Co and Cb₂Co₃, while the similar compounds over the Alloy will be (Cb-20Ta-15W-5Mo)₃Co and (Cb-20Ta-15W-5Mo)₂Co₃. Thicknesses of the cobalt-rich coatings vary from 0.05 to 6 mils, depending upon specific deposition conditions. Desired thicknesses for subsequent treatment are from about ½ to 2 mils.

In accordance with the invention, the second cycle comprises embedding the previously cobaltized columbium or Alloy substrates in aluminizing packs containing from about ½ to 15 percent, advantageously from about 1 to 5 percent, and preferably about 1 percent by weight of aluminum powder or flake; from about 0.05 to 3 percent, preferably about 1 percent of a powdered halide salt, and the balance an inert filter material, such as Al₂O₃. A most preferred mixture for the aluminizing has been found to be: about 1 percent aluminum by weight, about 1 percent halide salt by weight, and the balance inert refractory material. The aluminizing step may also be satisfactorily accomplished by using aluminum and an inert filler without a halide salt. These packs, contained in graphite cups, are then subjected to thermal exposure in an argon atmosphere at a temperature ranging from about 1600° to 2200° F. for times ranging from about ½ hour to 4 hours as required to form the desired thickness of CoAl coating (thicknesses between 0.1 and 5 mils were achieved). In accordance with the invention, it has been discovered that to develop the desired CoAl coatings, aluminizing must be carried out at temperatures greater than about 2000° F. At temperatures of 2000° F. and lower the CoAl structure tends to absorb an excessive amount of aluminum and thereby create compounds that are more aluminum rich than CoAl and which exist in liquid phase at temperatures as low as 2150° F. Such low melting compounds vitiate the desirable properties of the coating that are otherwise achieved with CoAl.

The procedures described above are representative of only one method by which CoAl coatings may be deposited upon columbium base substrates. The superior performance of the CoAl coatings abides in the composition and structure of the coating, and is not restricted to a pack cementation method of depositing the coating.

As to composition, chemical analyses have shown that the CoAl coatings derived from the pack cementation process may contain up to about 20 percent by weight of dissolved impurities, the principal among which are characteristically iron and tungsten, depending upon the specifics of the process. This may occur without significant alteration of physical structure and without detriment to the superior performance of these coatings.

For a clearer understanding of the invention, specific examples of the invention are given below. These examples are merely illustrative and are not to be understood as limiting the scope and underlying principles of the invention.

EXAMPLE 1

Coatings of CoAl were formed over specimens of ¼-inch diameter, ½-inch long unalloyed columbium using the above described two cycle pack cementation process. Cobaltizing was accomplished in graphite containers, using the following pack mixture:

15 percent by weight of cobalt powder;
3 percent by weight of NH₄Cl powder;
82 percent by weight of Al₂O₃ powder.

Treatment was for 8 hours at 2000° F. The resulting cobalt-rich coatings were 3 mils thick. The cobaltized specimens were then aluminized for 2 hours at 2200° F. in a graphite cup packed with the following mixture:

5 percent by weight of aluminum powder;
1 percent by weight of NaCl powder;
94 percent by weight of Al₂O₃ powder.

The resulting coatings consisted of a 2½ mil thick layer of CoAl containing a minor amount of dispersed CbAl₃ phase. Between this predominantly CoAl coating and the columbium substrate, a thinner layer of incompletely reacted cobalt-rich coating was observed.

One of the coated specimens was oxidized for 100 hours at 2200° F. During oxidation, the specimen was removed from the furnace and cooled to room temperature after 1.5, 3.0, 4.5, 20, 25, 50, 75, and 100 hours of cumulative time for weight measurement and visual examination. At no time during this test was coating failure observed. Cumulative specific weight gain during the oxidation exposure was 4.3 mg./cm.². Subsequent to this 100 hour-2200° F. oxidation exposure, the specimen was furnace-cooled from 2200° F. to room temperature, and was further oxidized for 28 hours (five heating and cooling cycles) at 1300° F. Although a local defect was initiated at a sharp corner of the specimen during exposure at 1300° F., no evidence of the rapid deterioration characteristic of trialuminide coatings on columbium base materials was observed.

By comparison, columbium, when aluminized to form 2- to 5-mil thick coatings of CbAl₃, is incapable of enduring more than four oxidation cycles (20 cycles) at 2200° F. without failure at local sites. Because CbAl₃ is a line compound having little solubility for its constituent elements, and thus exhibits less ductility than CoAl, it is unable to resist the repeated application of thermal cyclic stresses, in spite of its much superior thermal expansion match with columbium to that exhibited by CoAl.

EXAMPLE 2

Coatings of CoAl were formed over nominal ¼-inch diameter by ½-inch long rod specimens and nominal ⅜-inch square by ¼-inch thick tab specimens of

Cb-20Ta-15W-5Mo

alloy, using the 2 cycle pack cementation process. Cobaltizing was accomplished in steel containers using the following pack mixture:

15 percent by weight of cobalt powder;
6 percent by weight of NH₄Cl powder;
79 percent by weight of Al₂O₃ powder.

Treatment was for 4 hours at 2000° F. During this cobaltizing treatment, the packs were rotated at 1 revolution per minute. The resulting cobalt-rich coatings were 2 mils thick. The cobaltized specimens were then aluminized for 1 hour at 2200° F. in a graphite cup packed with the following mixture:

5 percent by weight of aluminum powder;
95 percent by weight of Al₂O₃ powder.

During aluminizing, the pack was rotated at 1 revolution per minute. The resulting coatings consisted of a continuous layer of CoAl, about 2 mils thick containing a minor amount of dispersed MAI₃ phase. Between this predominantly CoAl coating and the alloy substrate, a 1-mil thick layer of incompletely reacted cobalt-rich coating was observed.

A coated rod specimen was oxidized for 100 hours at 2200° F. in the same manner as described in Example 1. At no time during this test was coating failure observed. Cumulative specific weight gain during the oxidation exposure was 4.2 mg./cm.².

By comparison, columbium alloys, when aluminized to form 3- to 6-mil thick coatings of MAI₃ are generally incapable of enduring more than six or seven oxidation cycles (50 to 75 hours) without failure at local sites. In accordance with the invention, the superior ductility of CoAl permits it to better resist repeated thermal cyclic stresses than typical MAI₃ compounds, even though the latter possess superior thermal expansion match with respective alloys from which they are formed.

EXAMPLE 3

Coatings containing CoAl were formed over nominal ⅛-inch diameter by ½-inch long rod specimens and nominal ⅜-inch square by ¼-inch thick tab specimens of Cb-20Ta-15W-5Mo alloy, using the 2 cycle pack cementation process. Cobaltizing was accomplished in steel containers using the following pack mixture:

15 percent by weight of cobalt powder;
3 percent by weight of NH₄Cl powder;
82 percent by weight of Al₂O₃ powder.

Treatment was for 8 hours at 2000° F. During this treatment, the packs were rotated 180 degrees every 30 minutes. The resulting cobalt-rich coatings were 3 mils thick. The cobaltized specimens were then aluminized for 1 hour at 2200° F. in a graphite cup packed with the following mixture:

5 percent by weight aluminum powder;
1 percent by weight NaCl powder;
94 percent by weight Al₂O₃ powder.

During aluminizing, the pack was rotated 180 degrees every 30 minutes. The resulting coats were rough and irregular, but consisted primarily of about 4-mil thick CoAl over a thin incompletely reacted cobalt-rich layer intermediate between the CoAl layer and the substrate. The amount of MAI₃ phase contained in the CoAl coating was much greater than observed in either Example 1 or Example 2, and in several areas the continuity of the CoAl was disrupted by this MAI₃ phase.

A coated rod specimen was oxidized for 100 hours at 2200° F. in about the same manner described in Example 1. At no time during this test was coating failure observed. However, the cumulative specific weight gain during this test was 12.3 mg./cm.² or about three times the value exhibited by the coated specimens of Examples 1 and 2. Thus, although the coating of this example, which was heavily contaminated by the presence of MAI₃ phase, exhibited a capability for protecting the Alloy substrate for 100 hours at 2200° F., its oxidation performance was markedly inferior to that displayed by the relatively uncontaminated coatings of Examples 1 and 2.

Despite its inferior performance relative to the more perfect CoAl coatings of Examples 1 and 2, this MAI₃-contaminated coating, by virtue of the prominence of CoAl and its superior ductility, was able to resist the repeated thermal cyclic stresses of the test, thus demonstrating significant superiority over the MAI₃ class of coatings.

EXAMPLE 4

Coatings of CoAl were formed over rod and tab specimens of Cb-20Ta-15W-5Mo alloy using the 2 cycle pack cementation process. Cobaltizing was accomplished in packs as described in Example 2 by treating for 5 hours at 1800° F.; 1-mil thick cobalt-rich coatings resulted. An optional treatment after cobaltizing involved annealing in an argon atmosphere for 4 hours at 2000° F. Such cobalt-coated specimens, both with and without the optional heat treatment, were subsequently aluminized in a pack of the following mixture of powders.

1 percent by weight of aluminum;
1 percent by weight of NaCl;
98 percent by weight of Al₂O₃.

This pack, contained in graphite cups, was rotated at 1 r.p.m. during a 2-hour, 2200° F. aluminizing thermal exposure. CoAl coatings, about 1-mil thick, were formed. Residual cobalt-rich layers (not CoAl) up to about 1-mil thick existed between the CoAl and substrate material.

Coated rod specimens were oxidized for 100 hours at temperatures of 1300° and 2200° F. with thermal cycling between the test temperatures and room temperature as described in Example 1. The oxidation test results are summarized in Table 4 below:

Table 4

Processing Option	Oxidation Test Results			
	1,300° F.		2,200° F.	
	Coating Life, hours	Cumulative Specific Weight* Gain, mg./cm. ²	Coating Life, hours	Cumulative Specific Weight* Gain, mg./cm. ²
2,000° F. annealed.....	100	0.66	100	3.50
Not annealed.....	100	0.46	100	5.58

*After 100 hours at temperature.

No coating failures were observed during tests of these specimens, again demonstrating superior protective capability for CoAl coatings on columbium alloys. Furthermore, slow cooling from 2200° F. to about room temperature of the 100-hour, 2200° F.-exposed, 2000° F.-annealed processing option sample did not affect the coating to any measurable extent.

EXAMPLE 5

Coatings of CoAl were formed over nominal $\frac{3}{16}$ -inch diameter by 1-inch long rod specimens of Cb-20Ta-15W-5Mo alloy by the following procedure:

The specimens were electroplated to produce a 0.1-mil thick iron strike from a normal iron formate bath (pH 4.1), at 143° F. and 30 a.s.f. for five minutes. The specimens were then outgassed at 400° F. in a vacuum for 20 hours, which was followed by diffusing for one hour at 1300° F. in a vacuum. Further electroplating was next accomplished in a normal cobalt sulphate-chloride bath at about 30 a.s.f. and 115° F. for 15 minutes to produce a 0.5-mil cobalt electrodeposit. The second electrodeposition was followed by a flash plate for 10 minutes in a fused bath of 80 percent $AlCl_3$ by weight and 20 percent NaCl by weight at 325° F. and 40 a.s.f. Aluminizing was then accomplished by electroplating for 15 minutes in an ether hydride aluminum plating bath at room temperature and 30 a.s.f. to deposit a stoichiometric quantity of aluminum for subsequent reaction with the cobalt to form CoAl. The specimens were then encapsulated in a quartz under $\frac{1}{2}$ atmosphere of high purity argon. Finally, the specimens were heat treated to form the CoAl coating, as follows:

- (1) Heated to 1200° F. in 1½ hours and held for 4 hours.
- (2) Heated to 1250° F. in 20 minutes and held for 2 hours.
- (3) Heated to 1700° F. in 40 minutes and held for 15½ hours.
- (4) Heated to 1800° F. in 30 minutes and held for 1 hour.
- (5) Heated to 2000° F. in 30 minutes and held for 2 hours.
- (6) Heated to 2100° F. in 20 minutes and held for 2 hours.
- (7) Heated to 2200° F. in 30 minutes and held for 3 hours.
- (8) The capsule was air cooled to room temperature, broken open, and the specimens were removed.

After heat treatment, a small amount of powdery residue was observed on the specimens and on the inside of the quartz tube. The resultant CoAl coatings were

about ½-mil thick, and were covered with a thin (about 0.1-mil thick) unidentified layer.

A coated specimen was oxidation tested for 20 hours at 2200° F. This specimen was cooled to room temperature after 1.5, 3.0, 4.5, and 20 hours of accumulated time for weighing and visual examination. Weight gain during the first cycle (1.5 hours) was high because of oxidation of the thin, unidentified surface layer, but during the next two cycles (three hours) the specimen gained only 1 mg./cm.². This corresponded to a parabolic rate constant for oxidation of about 0.3 (mg./cm.²)²/hr., which compares well with the values of a 0.2 (mg./cm.²)²/hr. obtained for Examples 1 and 2. After 20 hours at 2200° F., this specimen had failed in several areas, and substrate oxidation was apparent.

Metallographic examination revealed practically no CoAl remaining in even the unfailed areas. Calculations indicate that consumption of ½-mil of CoAl by the combined processes of oxidation and interdiffusion with the substrate at 2200° F. would be complete within 20 hours of exposure time (about $\frac{2}{3}$ -mil would just suffice for complete protection for 20 hours at 2200° F.). In accordance with the invention, the specimens of this example obtained through electrodeposition of cobalt and aluminum on the substrate followed by heat treatment had an observed behavior that was consistent with the superior protective qualities of CoAl observed in Examples 1 and 2.

In summary, the novel coatings of this invention for columbium and columbium base alloy substrates achieve an important, new and useful result. Among the novel and unexpected beneficial results and advantages obtained from the coatings and methods for achieving the coatings of this invention are the following:

(1) As a coating compound, CoAl possesses a number of hitherto unappreciated intrinsic characteristics that make it particularly and unexpectedly beneficial as a coating material for columbium and columbium base alloy substrates. These characteristics include:

- (a) Its superior oxidation resistance and stability over the important temperature range up to at least about 2500° F., a temperature range within which the typical prior coatings such as, columbium aluminides, silicides, and beryllides, are subject to failure.
- (b) Its highly attractive diffusional stability when used as a coating for columbium and its alloys.
- (c) Its greatly superior ductility to prior coatings for columbium and its alloys at elevated temperatures.

(2) As a coating for columbium and its alloys, CoAl has both utility and practicality. In thicknesses of about 2 mils or more, it is capable of protecting columbium and columbium alloy substrates for times in excess of 100 hours at 2200° F.

(3) Importantly and unexpectedly, CoAl as a coating for columbium and its alloys is much less susceptible to thermal cyclic fatigue failure than the less ductile diffusion coatings, such as, those typified by $CbAl_3$ and MAI_3 , where M represents the proportionate ingredients of the substrate. In their possession of this important characteristic, CoAl coatings perform in a surprisingly beneficial manner, since they possess a relatively high level of thermal expansion mismatch with columbium and columbium alloy substrates. The discovery that CoAl provides a coating for columbium alloy substrates that is greatly superior to prior coatings in its resistance to thermal cyclic fatigue failure is one of the important attributes of the instant invention.

(4) The CoAl coatings of this invention are distinctly superior to prior coatings, such as, for example, the MAI_3 type of coatings, in that their low temperature oxidation resistance on columbium alloy substrates is not impaired by prior high temperature exposure.

(5) The CoAl coatings of this invention may be applied by different processes or methods and achieve virtually the same superior performance.

(6) Finally, the CoAl coatings of this invention have the capability of tolerating substantial contamination with foreign ingredients or phases without sacrificing or seriously impairing their protective function. Accordingly, CoAl is highly beneficial even when it only comprises a portion of the protective layer on columbium alloy substrates.

The invention in its broader aspects is not limited to the specific details shown and described, but departures may be made from such details within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

What is claimed is:

1. An article of manufacture having good stress-rupture strength at high temperatures, high temperature oxidation resistance, and resistance to cyclic fatigue failure, which comprises a core of metal selected from the group consisting of columbium and columbium base alloys, and a surface layer, adherently bonded to the core, consisting essentially of CoAl.

2. An article of manufacture having good stress-rupture strength at high temperatures, high temperature oxidation resistance, and resistance to cyclic fatigue failure, which consists essentially of a core of metal selected from the group consisting of columbium and columbium base alloys, and a coating adherently bonded to the core which consists essentially of a surface layer consisting essentially of CoAl and a sublayer consisting essentially of cobalt and the selected metal of the core, the sublayer being between the surface layer and the core.

3. A coated metal body comprising a substrate selected from the group consisting of columbium and columbium base alloys and having a protective surface layer adherently bonded to at least that part of substrate that is exposed to attack by oxygen at high temperatures, the surface layer comprising predominantly CoAl and being ductile, cyclic fatigue resistant, and diffusionally stable.

4. A coated metal body comprising a substrate selected from the group consisting of columbium and columbium base alloys and a protective coating adherently bonded to at least that part of the substrate that is exposed to attack by oxygen at high temperatures, the coating having a surface layer comprising predominantly CoAl and a

sublayer between the surface layer and the substrate consisting essentially of cobalt and the selected metal of the substrate, said coating being ductile, cyclic fatigue resistant, and diffusionally stable.

5. An article of manufacture having good stress-rupture strength at high temperatures, high temperature oxidation resistance, and resistance to cyclic fatigue failure, which comprises a core of metal selected from the group consisting of columbium and columbium base alloys and an oxidation protective surface layer adherently bonded to the core, the surface layer comprising predominantly CoAl and a metal dissolved in the CoAl, the dissolved metal being at least one of cobalt in an amount of up to 30 atomic percent in excess of the stoichiometric quantity of cobalt in the CoAl or aluminum in an amount of up to 2 atomic percent in excess of the stoichiometric quantity of aluminum in the CoAl.

6. The article of claim 1 in which the dissolved metal is cobalt in an amount of up to about 30 atomic percent in excess of the stoichiometric quantity of cobalt in the CoAl.

7. The article of claim 1 which has a sublayer located between the surface layer and the core, the sublayer consisting essentially of cobalt and the selected metal of the substrate.

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