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COATINGS FOR COLUMBIUM BASE ALLOYS

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2 Sheets-Sheet 1

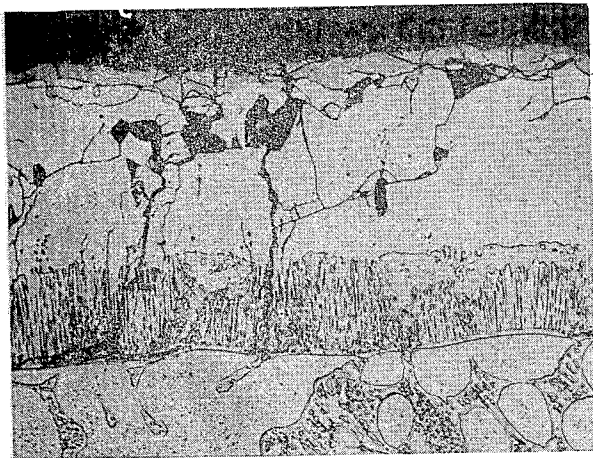


**FIG. 1**

CoSi<sub>2</sub> STRUCTURE

Co-MODIFIED  
Cb-Si<sub>2</sub> STRUCTURE

SUBCOATING ZONE

Cb-14Co SUBSTRATE

SILICIDE COATING DEPOSITED OVER Cb-14 Co SUBSTRATE  
500X MAGNIFICATION

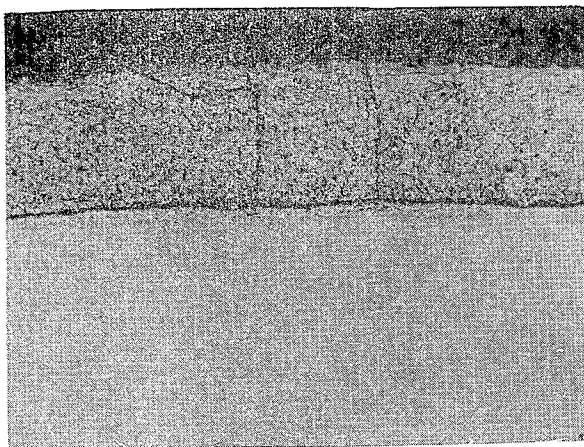


**FIG. 2**

CoSi<sub>2</sub> PHASE

CoSi SUBSURFACE AND  
DISPERSED PHASE;  
MATRIX IS MSi<sub>2</sub>-TYPE  
PHASE

SUBSILICIDE

Cb-20Ta-15W-5Mo  
SUBSTRATE

COBALT-SILICIDE COATING OF TYPE B ON Cb-20Ta-15W-5Mo  
500 X MAGNIFICATION

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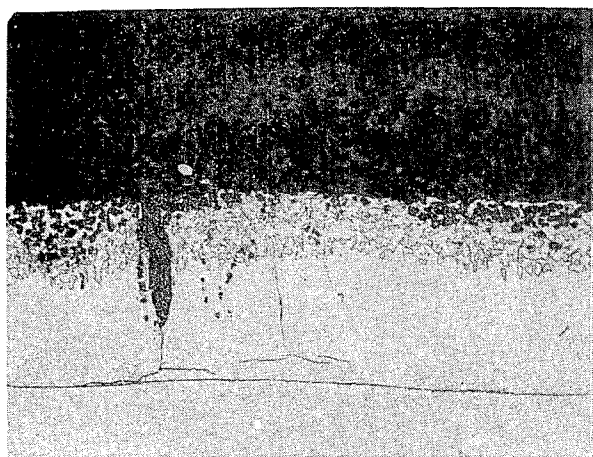


**FIG. 3**

COMPLEX OXIDE

CoSi MATRIX  
CONTAINING MSi<sub>2</sub>  
PARTICLES

MSi<sub>2</sub>

DIFFUSION ZONE  
(SUBSILICIDES)

ALLOY SUBSTRATE

COBALT-SILICON COATING OVER Cb-20Ta-15W-5Mo ALLOY AFTER CYCLIC  
OXIDATION FOR 100 HRS AT 2300° F  
500X MAGNIFICATION

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## COATINGS FOR COLUMBIUM BASE ALLOYS

Elihu F. Bradley, West Hartford, Conn., and Edwin S. Bartlett, Worthington, and Horace R. Ogden and Robert I. Jaffee, Columbus, Ohio, assignors, by direct and mesne assignments, to United Aircraft Corporation, East Hartford, Conn., a corporation of Delaware  
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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 cobalt-silicon coatings (such as,  $\text{CoSi}_2$ ,  $\text{CoSi}$  and combinations thereof) for columbium and its alloys in which the coatings may be created by methods, such as, vapor deposition, flame or plasma torch spraying, slurry application techniques, electrophoretic deposition, hot pressure bonding, and the like, and to a method for obtaining vapor deposition of such cobalt-silicon coatings on columbium base materials to produce a protective layer over the base metals of the alloys that provides an oxidation-resistant coating for the base metal at very high temperatures, such as, for example, temperatures up to at least  $2400^\circ\text{F}$ .

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  $1600^\circ$  and  $1900^\circ\text{F}$ .

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 ( $4380^\circ\text{F}$ ) 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  $4380^\circ\text{F}$ , pure columbium becomes too weak for practical structural use at temperatures above  $1200^\circ\text{F}$ . 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 resist-

ance and high-temperature strength through alloying alone. Since the major fields of utility for columbium base alloys depend largely upon retention of high-temperature 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 typically hard and brittle and are thus subject to cracking or other failure at localized sites. In contrast to molybdenum, which oxidizes catastrophically, however, the oxide of columbium does not volatilize; 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  $2400^\circ\text{F}$ . (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  $1000^\circ\text{F}$  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  $1000^\circ\text{F}$  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,  $\text{NaCl}$ ,  $\text{KF}$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{Cl}$ , and the like), and an inert filler material (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{BeO}$ ,  $\text{MgO}$ , 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 may be used to produce controlled-thickness coatings on colum-

bium, the major proportions of which may be compounds, such as,  $\text{CbAl}_3$ ,  $\text{CbSi}_2$ , 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  $1300^\circ\text{F.}$ ) or at high temperatures (greater than about  $2000^\circ\text{F.}$ ). Perhaps the most serious deficiency of existing coatings for columbium, however, is their propensity for failure at localized sites. For technological reasons, silicide coatings on columbium and its structural alloys are less susceptible to localized failures than are aluminide or beryllide coatings, and are thus of primary interest. Silicide coatings on structural columbium alloy substrates, however, are prone to rapid consumption by oxidation at "low" (about  $1300^\circ\text{F.}$ ) temperatures (this characteristic of silicide coatings is sometimes termed "the silicide pest phenomenon") and at "high" (about  $2000^\circ\text{F.}$  or higher) temperatures. Modification of silicide coatings is thus highly desirable to impart sufficient longevity to give to them a utility they do not normally possess.

Copending application Serial No. 65,962, filed October 31, 1960, now abandoned, 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  $2500^\circ\text{F.}$  Typical of this latter class of alloys is the composition  $\text{Cb-20Ta-15W-5Mo}$  (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 at least about  $2300^\circ\text{F.}$ , and preferably to at least about  $2400^\circ\text{F.}$ , and that will achieve cobalt-silicon compound coatings that are highly resistant to failure at localized sites.

Another object of this invention is to provide a coating for columbium and alloys thereof that overcomes the silicide and aluminide pest phenomenon characterized by rapid consumption of silicide and aluminide coatings through oxidation at temperatures of about  $1300^\circ\text{F.}$ , and also overcomes rapid consumption of aluminide and silicide coatings through oxidation at high temperatures of about  $2000^\circ\text{F.}$  or higher and provides a coating that gives excellent oxidation resistance at temperatures up to at least about  $2200^\circ\text{F.}$ , and in preferred forms of the invention to temperatures up to at least about  $2300^\circ\text{F.}$  and  $2400^\circ\text{F.}$

Further objects of this invention are to provide a coating for columbium and alloys thereof that in addition to providing resistance to simple thermal oxidation will also be protective under other reasonably expected conditions of use, and to this end, the protective coatings of this invention achieve good resistance to thermal cycling, thermal shock, formation of defects and high velocity gas erosion.

Other objects of this invention are to provide for columbium and its alloys: (1) a coating that in nominal thicknesses of 2 mils or more is capable of providing protection for exposures to high temperature oxidizing environments for times in excess of 100 hours at temperatures up to at least about  $2200^\circ\text{F.}$  and in preferred forms at temperatures up to at least about  $2300^\circ\text{F.}$  and  $2400^\circ\text{F.}$ ; (2) a coating that exhibits excellent resistance to thermal shock failure; (3) a coating that displays excellent resistance to the formation of defects at both higher and lower temperatures of exposure; (4) a coating that achieves significant resistance to high velocity gas erosion; (5) a coating that is relatively insensitive to the process by which it is applied to columbium alloy substrates; and (6) a coating that is relatively insensitive to substrate geometry effects.

A further object of this invention is to provide a cobalt-silicon coating for columbium and its alloys that includes as a sublayer or subzone a disilicide of the sub-

strate that acts as a thermal expansion buffer and prevents any failure of the coating due to thermal expansion mismatch between the cobalt-silicon compounds of the coating and the substrate.

Still further objects of this invention are to provide a method for coating columbium and its alloys with cobalt-silicon compound coatings using a vapor deposition (pack-cementation) process that will achieve substantial uniformity of the coating and yield an essentially uniform coating on even intricately shaped parts and at the edges and corners of parts and to provide further a method for depleting the low-melting  $\text{CoSi}_2$  component of the cobalt-silicon compound coatings to improve the maximum-temperature capability of the coatings.

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 includes a columbium base substrate having good stress-rupture strength at high temperatures and good resistance to oxidation at temperatures up to  $2200^\circ\text{F.}$  or higher and having a coating comprising cobalt and silicon wherein substantially all of the cobalt is stoichiometrically combined with the silicon to form at least one compound selected from the group consisting of  $\text{CoSi}$  and  $\text{CoSi}_2$ . The coating may also include excess silicon over that required to combine stoichiometrically with the cobalt, the excess silicon being combined with the metal of the substrate in the form of at least one compound selected from the group consisting of a disilicide of the substrate and subsilicides of the substrate.

The invention may also be described as including a new and improved article of manufacture having good stress-rupture strength at high temperatures, high temperature oxidation resistance, and resistance to cyclic fatigue failure, which article comprises a core of metal selected from the group consisting of columbium and alloys thereof, the article having a thermal cyclic failure resistant, defect resistant, and broad range oxidation-resistant coating or surface zone consisting essentially of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$ , and mixtures thereof. In one form, the coating may consist essentially of an outer layer or zone of  $\text{CoSi}_2$ , an intermediate layer or zone consisting essentially of  $\text{CoSi}$  dispersed in a matrix of a disilicide of the substrate and an inner layer or zone consisting essentially of a disilicide of the substrate over subsilicides of the substrate. In a preferred form of the invention, the coating consists essentially of a  $\text{CoSi}$  surface layer or zone over a layer or zone consisting essentially of  $\text{CoSi}$  dispersed in a matrix of a disilicide of the substrate, which in turn is over a layer or zone of one or more subsilicides of the substrate.

This invention also embraces as an article of manufacture, a refractory metal body, comprising a substrate selected from the group consisting of columbium and its alloys and having an exterior exposed layer or zone composed predominately of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$  and mixtures thereof, and having a sublayer or zone beneath the exterior exposed layer or zone composed predominately of at least one compound selected from the group consisting of  $\text{CoSi}$ , a disilicide of the substrate, and mixtures thereof, the body being characterized by good stress-rupture strength at high temperatures and good resistance to oxidation at temperatures up to about  $2400^\circ\text{F.}$

In accordance with its purpose, this invention includes a method of producing a coated metal article having resistance to oxidation at high temperatures and a good stress-rupture strength at high temperatures, which method

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comprises depositing a surface coating on a metal substrate, the substrate being a metal selected from the group consisting of columbium and alloys thereof, and the coating consisting essentially of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$ , and mixtures thereof.

In another form, the method may comprise depositing a coating on a metal substrate, the substrate being a metal selected from the group consisting of columbium and its alloys, and the coating having a surface layer consisting essentially of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$ , and mixtures thereof, and the coating having a sublayer or subzone consisting essentially of at least one compound selected from the group consisting of  $\text{CoSi}$ , a disilicide of the substrate, mixtures thereof, and one or more subsilicides of the substrate.

One embodiment of such method includes a two-cycle vapor deposition process of coating a fabricated base metal which process comprises surrounding a base metal selected from the group consisting of columbium and its alloys with a powdered pack of a finely ground source of cobalt and a small amount of a volatilizable ammonium halide salt as active ingredients and an inert filler, heating the base metal and powdered pack for a time period sufficient to cause volatilization of the ammonium halide salt and to produce deposition of elemental cobalt on the surface of the base metal, then surrounding the cobaltized base metal with a powdered pack of a finely ground source of silicon and a small amount of a volatilizable halide salt as active ingredients and an inert filler, heating the base metal for a time period sufficient to cause volatilization of the halogen in the halide salt and to effect the creation of an exterior surface layer or zone on the base metal composed predominately of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$ , and mixtures thereof. The coating on the base metal may also have a subsurface layer or zone composed predominantly of at least one compound selected from the group consisting of  $\text{CoSi}$ , a disilicide of the base metal, mixtures thereof, and one or more subsilicides of the base metal. The subsurface layer or zone preferably consists essentially of  $\text{CoSi}$  as a dispersed phase in a matrix of a disilicide of the base metal either with or without a disilicide of the base metal in a zone between the  $\text{CoSi}$  layer and the base metal and a subsilicide of the base metal in a zone between the base metal or substrate and the zone occupied by the disilicide of the base metal.

Although it has been found that for pack cobaltizing best results are achieved when an ammonium halide salt is used, such as, ammonium chloride ( $\text{NH}_4\text{Cl}$ ), cobaltizing may alternatively be accomplished by using the complexed compound cobaltic hexammine chloride



salt as the active ingredient in the cobaltizing pack mix. Moreover, although it is possible to achieve pack cobaltizing using sodium halide salts, such as  $\text{NaCl}$  and  $\text{NaI}$ , and particularly  $\text{NaF}$ , the reaction proceeds at too slow a rate to yield a truly practical method.

This invention also includes within its scope a method of depleting  $\text{CoSi}_2$  from the exterior surface layer or zone to create an exterior surface layer or zone that is composed predominantly of  $\text{CoSi}$  over the substrate. The depletion of the lower-melting  $\text{CoSi}_2$  component of the cobalt-silicon coating improves the maximum temperature capability of the coating as a whole, since the  $\text{CoSi}$  that remains after depletion of  $\text{CoSi}_2$  maintains its solid phase up to temperatures more than  $200^\circ\text{F}$ . higher than the melting point of  $\text{CoSi}_2$ .

One method of depleting the  $\text{CoSi}_2$  component of the cobalt-silicon coating obtained by depositing a cobalt-silicon coating on a substrate of columbium and its alloys (such as, by a pack-cementation vapor deposition process)

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is the method which comprises preoxidizing the cobalt-silicon coating by heating the coated substrate in an atmosphere containing oxygen to a temperature of from about  $1800^\circ$  to  $2300^\circ\text{F}$ ., preferably to about  $2200^\circ\text{F}$ ., for times sufficient to complete substantial depletion of the  $\text{CoSi}_2$ . Such preoxidizing at elevated temperatures promotes selective oxidation attack on the  $\text{CoSi}_2$ , thereby removing it and leaving a predominantly  $\text{CoSi}$  phase as a preferred embodiment of a continuous coating for the substrate that imparts a higher maximum temperature capability.

Other methods within the scope of this invention that can be used to remove a deposited  $\text{CoSi}_2$  coating when higher maximum temperature capabilities are desired are (1) selective chemical etching; (2) machining; (3) vapor or sand blasting; (4) heating under a vacuum; (5) removal by a decomposition reaction. It is thus apparent that various suitable physical, chemical, metallurgical or mechanical methods for depleting the  $\text{CoSi}_2$  component of the coating may be used to achieve an exterior surface layer or zone that is predominately composed of  $\text{CoSi}$ .

As previously set forth, conventional silicide and aluminide coatings on structural columbium alloy substrates are prone to rapid consumption through oxidation at low (about  $1300^\circ\text{F}$ .) temperatures (this tendency is sometimes referred to as the pest phenomenon) and at high (about  $2000^\circ\text{F}$ . or higher) temperatures. At the latter temperature a rapid oxidation mechanism occurs which though different from the pest phenomenon, is similar in its undesirable end result.

Quite unexpectedly, and contrary to what one would expect from the usual behavior of silicide coatings, if the cobalt-silicon coatings of this invention are used on columbium and columbium alloy substrates, the deleterious effects of both the low temperature pest phenomenon and high temperature rapid oxidation mechanism are essentially overcome. The cobalt-silicon coatings of the present invention are thus particularly outstanding in their ability to protect columbium and its alloys from oxidation under a wide variety of conditions of use and at temperatures that run the gamut up to at least about  $2200^\circ\text{F}$ ., and in preferred forms of this invention up to temperatures of at least about  $2300^\circ$  and  $2400^\circ\text{F}$ . These coatings possess distinctly superior oxidation resistance and superior defect resistance up to at least about  $2400^\circ\text{F}$ . and overcome the tendency of cobalt-free silicide coatings on columbium substrates to fail at the critical temperatures of about  $1300^\circ\text{F}$ . and about  $2000^\circ\text{F}$ . or above.

Also, quite surprisingly, localized coating failure, an intrinsic deficiency of most brittle intermetallic coatings, is minimized by the cobalt-silicon coatings of this invention in spite of a relatively high thermal expansion mismatch between the coatings and the substrate. It has been found that when the coatings of this invention are applied to columbium base substrates by the methods of this invention, a disilicide of the substrate metal forms either as a continuous phase or matrix for the compound  $\text{CoSi}$  as a dispersed phase, or as a dispersed phase in a  $\text{CoSi}$  matrix, and it also characteristically forms a sublayer or subzone beneath the  $\text{CoSi}$  zone. Further, in accordance with the invention, the subzone composed of the disilicide of the metal substrate acts as a thermal expansion buffer between the outer zones of the coating and the substrate, since the disilicides possess thermal expansion properties intermediate those of the substrate and the outer zones of the coating.

The oxidation resistance of the two cobalt-silicon compounds considered to have potential as coatings for columbium alloys was examined by preparing the desired materials,  $\text{CoSi}_2$  and  $\text{CoSi}$ , in massive form by tungsten-electrode-arc melting. Specimens of these compounds were oxidation tested in air for 100 hours at temperatures of  $1300^\circ$  and  $2200^\circ\text{F}$ . The results of these oxidation

tests are compared with those of similar tests upon the compound CbSi<sub>2</sub> in Table 1 below:

TABLE 1

| Compound                | Oxidation Temperature, °F. | Oxidation Time, hr. | Weight Gain mg./cm. <sup>2</sup> |
|-------------------------|----------------------------|---------------------|----------------------------------|
| CbSi <sub>2</sub> ----- | 1,300                      | 25                  | 182                              |
|                         | 2,200                      | 25                  | 177                              |
| CoSi <sub>2</sub> ----- | 1,300                      | 100                 | -0.1                             |
|                         | 2,200                      | 100                 | 0.3                              |
| CoSi-----               | 1,300                      | 100                 | -0.2                             |
|                         | 2,200                      | 100                 | -0.1                             |

From these data, it can be seen that both cobalt-silicon compounds exhibit decidedly superior oxidation-resisting potential as coatings compared to that of unmodified CbSi<sub>2</sub>-CoSi<sub>2</sub> melts at a temperature of 2331° F., and the protection afforded by this structure is thus limited to temperatures up to about 2300° F. In contrast, however, the CoSi structure remains solid up to 2580° F. and thus exhibits a potential for coating protection to temperatures up to at least about 2400° F.

The auspicious nature of cobalt-silicon compound coatings for columbium and its alloys was further demonstrated by modifying silicide coatings produced during pack siliconizing of propitiously modified columbium alloy substrates. Silicide coatings having the desired modifications were produced by proportionate reaction with a modified substrate alloy that occurs during the pack-cementation process. Pack siliconizing was accomplished by embedding chemically cleaned specimens to be coated in a particulate mixture consisting of:

- 17 percent by weight of silicon powder,
- 3 percent by weight of NaF powder,
- 80 percent by weight of Al<sub>2</sub>O<sub>3</sub> powder.

These packs, contained in covered steel cans, were then exposed in an argon atmosphere to a temperature of 2200° F. for about 4 hours. The specimens were cooled, removed from the pack, repacked in a fresh pack mixture of the same composition, and exposed for an additional 12 hours at 2200° F. under argon.

A columbium alloy substrate consisting essentially of 86 percent by weight of columbium and 14 percent by weight of cobalt (Cb-14Co), when treated in the foregoing manner, developed a coating that was 4.5 mils thick. In addition to the expected modification of the disilicide (i.e., CbSi<sub>2</sub>) phase by the substrate, the resultant coating displayed a ½ mil thick foreign surface phase which was determined by X-ray diffraction and metallographic techniques to possess the CoSi<sub>2</sub>-phase structure. FIG. 1 is a photomicrograph showing this coating enlarged 500 times and showing that it possesses a structural novelty that sets it apart from other typical modified silicide coatings. The CbSi<sub>2</sub> structure underlying the CoSi<sub>2</sub> structure was modified by the presence of about 1 percent by weight of cobalt.

Oxidation tests were conducted in air at temperatures of 1300° and 2200° F. on the CoSi<sub>2</sub>-containing coatings. During these tests, specimens were cycled between the test temperature and room temperature eight times. Accumulated time at each exposure temperature was 100 hours. The test results are compared with results of similar tests on CbSi<sub>2</sub>-coated columbium in Table 2 below:

TABLE 2

|                                    | Oxidation Temperature, °F. | Coating Life, hr. | Weight Change, mg./cm. <sup>2</sup> |
|------------------------------------|----------------------------|-------------------|-------------------------------------|
| CbSi <sub>2</sub> -----            | 1,300                      | 20                | 1-1.4                               |
| CoSi <sub>2</sub> -containing----- | 1,300                      | >100              | 0.1                                 |
| CbSi <sub>2</sub> -----            | 2,200                      | 75                | 30.4                                |
| CoSi <sub>2</sub> -containing----- | 2,200                      | >100              | 6.3                                 |

<sup>1</sup> Coating powdered.

In accordance with the invention and as shown by the data in Table 2, the protection afforded to the columbium base substrate by the coating that contains the CoSi<sub>2</sub> phase is far superior to that of the unmodified CbSi<sub>2</sub> coating at both of the critical (relative to CbSi<sub>2</sub> coatings) temperatures of 1300° and 2200° F. Similar coatings over a Cb-3Co (columbium-3 weight percent cobalt) alloy substrate exhibited only very thin and discontinuous CoSi<sub>2</sub> phase and relied upon essentially the cobalt-modified CbSi<sub>2</sub> structure for the protection of the substrate. Oxidation tests of these coatings showed lives of less than 20 hours at 1300° F. and less than 75 hours at 2200° F., thus behaving similarly to unmodified CbSi<sub>2</sub> coatings. These tests demonstrate that the superior behavior of this siliconized Cb-14Co alloy system was attributable to the CoSi<sub>2</sub> phase and not to cobalt modification of the CbSi<sub>2</sub> structure.

For a clearer understanding of the invention, specific examples of the invention are set forth in this specification. These examples are merely illustrative and are not to be understood as limiting the scope and underlying principles of the invention.

In the embodiments forming the examples of this invention a Cb-20Ta-15W-5Mo alloy was selected as a representative substrate material. Other columbium-base alloys, such as those taught in copending application Serial No. 65,962, filed October 31, 1960, could have been used equally well as substrates to illustrate the new and desirable performance of the cobalt-silicon coatings for columbium and its alloys described in this specification.

Cobalt-silicon coatings were applied to the Cb-20Ta-15W-5Mo substrate, hereafter referred to as "the alloy," by utilizing a two-cycle pack-cementation process, in which the first cycle comprised embedding chemically cleaned and polished specimens to be coated in a cobaltizing pack of the following mixture:

- 15 percent by weight cobalt powder,
- 6 percent by weight NH<sub>4</sub>Cl powder,
- 79 percent by weight Al<sub>2</sub>O<sub>3</sub> powder.

It was found that cobaltizing could be accomplished successfully in packs containing from 5 to 50 percent cobalt, preferably from 15 to 30 percent cobalt, and from 1 to 15 percent NH<sub>4</sub>Cl, preferably 3 to 9 percent. The packs, contained in covered steel cans or graphite cups, were then subjected to various thermal treatments ranging from 1400° to 2200° F. for times of from about 1 to 24 hours, advantageously from 1.5 to 8 hours, and preferably from 2 to 6 hours, as required to deposit a desired amount of cobalt. In accordance with the invention, the packs were usually rotated at a speed of 1 r.p.m during the thermal treatment to assure uniform coating and reaction of the Alloy with cobalt.

During this treatment, cobalt reacted to some extent with the substrate to form, for example, compounds such as M<sub>3</sub>Co or M<sub>2</sub>Co<sub>3</sub> or other cobalt-rich layers at the surface, where M represents about the proportionate ingredients as they occur in the substrate. For example, the cobalt-rich coating over the Alloy was found by electron beam microprobe analytical techniques to contain predominately two phases, MCo<sub>2</sub> and a cobalt solid solution phase containing about 10 percent by weight of substrate elements Cb, Ta, W, Mo (and also some iron as this particular coating was cobaltized in a steel pack).

Thicknesses of the cobalt-rich coatings varied from 0.1 to 6 mils depending on specific deposition conditions. Desired thicknesses of cobalt-rich coatings for subsequent treatment were from about ½ to 2 mils. In particular, two cobaltizing treatments were used successfully as the first step in developing the desired cobalt-silicon coating structures. These were the treatments shown under I and II of Table 3 below:

TABLE 3

| Pack composition.....                    | Cobaltizing Process                                                   |                                                                       |
|------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------|
|                                          | I                                                                     | II                                                                    |
| Temperature, ° F.....                    | 2,000                                                                 | 1,800                                                                 |
| Time, hr.....                            | 8                                                                     | 1.5                                                                   |
| Cobalt-rich coating thickness, mils..... | 2                                                                     | 1/2                                                                   |
|                                          | 15% Co<br>3% NH <sub>4</sub> Cl<br>82% Al <sub>2</sub> O <sub>3</sub> | 15% Co<br>5% NH <sub>4</sub> Cl<br>79% Al <sub>2</sub> O <sub>3</sub> |

The second coating cycle consisted of embedding the previously cobaltized alloy substrates in siliconizing packs containing at least about 3 percent by weight, and preferably from 10 to 30 percent, silicon powder; from 1 to 10 percent by weight, and preferably about 3 percent, NaF powder; and the balance essentially Al<sub>2</sub>O<sub>3</sub> powder. These packs, contained in steel cups, were then subjected to thermal exposure in an argon atmosphere at temperatures of from about 2000° to 2400° F. for times ranging from 2 to 4 hours. Total thicknesses of the resulting cobalt-silicon coatings ranged from 2 to 4 mils, depending on the coating conditions. In particular, cobalt-rich coatings produced by cobaltizing Process I were subsequently siliconized for from 1 to 24 hours, preferably 2 to 4 hours, and resulted in cobalt-silicon coatings that were about 2 to 8 mils, preferably 2 to 3 mils, thick respectively. Cobalt-rich coatings of Process II were siliconized for about 3 to 4 hours and coating thicknesses in this instance were about 3 mils. For convenience in tabulating data, these cobalt-silicon coatings are referred to as:

- A.—Cobalt Process I, 2 hour siliconizing,  
B.—Cobalt Process I, 4 hour siliconizing,  
C.—Cobalt Process II, 4 hour siliconizing.

Other appropriate siliconizing treatments could, of course, have been used to develop the desired cobalt-silicon coatings.

The second coating cycle for producing A, B and C above, comprised embedding the previously cobaltized alloy substrates in siliconizing packs containing in weight percent:

- 17 percent silicon powder,  
3 percent NaF powder,  
80 percent Al<sub>2</sub>O<sub>3</sub> powder.

These packs, contained in covered steel cans, were then subjected to various thermal exposures in an argon atmosphere at a temperature of about 2200° F. for times ranging from 2 to 4 hours depending on the process being followed, A, B or C.

FIG. 2 is a photomicrograph showing a typical cobalt-silicon coating on the Alloy enlarged 500 times. As shown in FIG. 2, the CoSi<sub>2</sub> phase is present as a thin, 0.2 to 0.5 mil thick, continuous surface layer. Underneath the surface phase of CoSi<sub>2</sub> is a second cobalt-silicon compound, CoSi (identified by X-ray diffraction analysis). This CoSi compound exists as a continuous subsurface phase and also is dispersed throughout the underlying matrix of CbSi<sub>2</sub> (proportionately modified with Ta, W, and Mo, and also containing some cobalt).

Coatings produced by all three processes (A, B, and C) displayed the same general features and contained significant amounts of either CoSi or CoSi<sub>2</sub> phases, or both of these, as well as the modified CbSi<sub>2</sub> phase. Processing did alter the relative amounts of the various phases such that in some coatings the surface phase of CoSi<sub>2</sub> was very thin and discontinuous, but these alterations were of minor importance to the resultant oxidation behavior. Thus, the cobalt-silicon coatings prepared by the two-cycle coating process typically contain substantial amounts of the oxidation resistant compounds, CoSi and/or CoSi<sub>2</sub>.

Oxidation resistance of such cobalt-silicon coatings on the alloy was evaluated by standard cyclic oxidation tests in air at temperatures of 1300°, 2200°, 2300°, and 2500° F. Time intervals for cyclic exposures were as shown in Table 4 below:

TABLE 4

| Cycle | Time for Cycle, hr. | Cumulative Time, hr. |
|-------|---------------------|----------------------|
| 1     | 1.5                 | 1.5                  |
| 2     | 1.5                 | 3.0                  |
| 3     | 1.5                 | 4.5                  |
| 4     | 15.5                | 20.0                 |
| 5     | 5                   | 25                   |
| 6     | 25                  | 50                   |
| 7     | 25                  | 75                   |
| 8     | 25                  | 100                  |

The most significant results of these tests are summarized in Table 5. These data show remarkable superiority for these cobalt-silicon coatings over the behavior of CbSi<sub>2</sub> coatings at temperatures to at least 2200° F. In accordance with the invention, at 2200° F. the performance of these coatings, which contained doubly protective layers of both CoSi and CoSi<sub>2</sub>, judged by weight-gain data, was superior to specimens where CoSi<sub>2</sub> alone imparted improved oxidation behavior, as cited previously. At temperatures above the melting point of the CoSi<sub>2</sub> phase and approaching that of the CoSi phase, protective capacity of these cobalt-silicon coatings is reduced; however, it has been found that this deficiency can be overcome through depletion and removal of the CoSi<sub>2</sub> phase by pre-oxidizing, or by another appropriate method, to leave only the higher melting CoSi phase, thereby giving to the coating a higher maximum temperature capability.

TABLE 5.—OXIDATION TEST RESULTS OF COBALT-SILICON COATINGS ON Cb-20Ta-15W-5Mo COLUMBIUM ALLOY

| Oxidation Temperature, ° F. | Coating Process | Coating Life, hr. | Weight Change During Test, mg./cm. <sup>2</sup> |
|-----------------------------|-----------------|-------------------|-------------------------------------------------|
| 1,300                       | A               | >100              | 0.60                                            |
| 1,300                       | B               | >100              | 0.40                                            |
| 2,200                       | A               | a 25              | 0.77                                            |
| 2,200                       | A               | >100              | 1.7                                             |
| 2,200                       | B               | >100              | 1.7                                             |
| 2,200                       | B               | b >60             | 0.8                                             |
| 2,300                       | B               | >100              | 3.6                                             |
| 2,300                       | C               | >100              | 5.3                                             |
| 2,500                       | B               | 20                | (c)                                             |
| 2,500                       | C               | a 25              | -5.2                                            |

a Local defect failure.

b Furnace burnout; test stopped.

c Specimen destroyed by oxidation.

Oxidation tests at 2400° F. showed results to be no better than those obtained at 2500° F.

In accordance with the invention, localized coating failure, an intrinsic deficiency of most brittle intermetallic coatings, is minimized by the cobalt-silicon coatings of this invention. Of the eight coated specimens tested at temperatures from 1300° to 2300° F., only one developed a local defect in times up to 100 hours at temperature. No particular precautions regarding edge preparation of specimens were followed, emphasizing the resistance of cobalt-silicon coatings to local defect failures.

By comparison, with unmodified silicide coatings in specimens similar in design to the examples of this invention, local defect failure occurs in less than 100 hours about 40 percent of the time; such failures are even more frequent with unmodified aluminide coatings. The data of Table 5 further demonstrate the insensitivity of coating behavior to minor variations in the coating process—the specimens used for the oxidation tests were coated by different procedures but still performed equally well. Reproducibility of coating behavior is excellent. Although not indicated in Table 5, the cobalt-silicon coatings of this invention are insensitive to the geometry of the coated alloy substrate—cobalt-silicon coatings in both alloy rod

(1/8 to 1/4-inch diameter) and sheet (0.06 inch thick) specimens behaved equally well in oxidation tests.

A specimen that had been cobalt-silicon coated by process B and oxidized without failure for 60 hours at 2200° F. was cooled from 2200° F. to about 500° F. over a period of five hours with no deterioration of the coating. This specimen was again reheated to 2200° F. and slow cooled in the same manner, again with no detrimental effects. By comparison, unmodified disilicide (CbSi<sub>2</sub>) or trialuminide (CbAl<sub>3</sub>) coatings are unable to sustain even one slow-cooling cycle after similar high temperature exposure and disintegrate completely under these conditions.

As an example of another form of this invention, the alloy in a chemically cleaned and polished specimen was embedded in a cobaltizing pack of the following mixture:

15 percent by weight of cobalt powder,  
6 percent by weight of NH<sub>4</sub>Cl powder,  
79 percent by weight of Al<sub>2</sub>O<sub>3</sub> powder.

The pack, contained in a covered steel can, was then subjected to thermal exposure in an argon atmosphere at a temperature of about 1700° F. for 12 hours. During this cobaltizing treatment, the pack was rotated at 1 revolution per minute. The resulting cobalt-rich coating was about 1.2 mils thick. This cobaltized specimen was then siliconized by embedding it in a pack of the following mixture:

17 weight percent silicon powder,  
3 weight percent NaF powder,  
80 weight percent of Al<sub>2</sub>O<sub>3</sub> powder.

This pack, in a graphite container, was then subjected to thermal exposure in an argon atmosphere at a temperature of about 2000° F. for two cycles. The first cycle was about 12 hours in duration and the second about 4 hours. During siliconizing, the pack was rotated at 1 revolution per minute. The resulting coating consisted of a continuous layer or zone of CoSi<sub>2</sub>, a sublayer or subzone of CoSi, and a layer or zone beneath the sublayer consisting essentially of a disilicide of the substrate. The coating layer was about 3.2 mils thick. Finally, there was an innermost layer or zone constituting a subsilicide of the substrate.

In accordance with the invention, and as an illustration of the preferred form of this invention, the specimen of the foregoing example was subjected to a preoxidation treatment for depletion of the low-melting CoSi<sub>2</sub> component of the cobalt-silicon coating thereby to improve the maximum temperature capability of the coating. The specimen was oxidized at 2200° F. for 300 hours using 16 cycles; it gained a total of only 3.1 mg./cm.<sup>2</sup>, and no coating failure occurred. This specimen was then oxidized at 2400° F. for 95.5 additional hours using 5 more cycles as set forth in Table 6 below. During this oxidation treatment at 2400° F. the specimen gained only 1.17 mg./cm.<sup>2</sup>. No coating failure occurred.

TABLE 6

| Cycle | Time at 2,400° F., hr. | Weight Gain, mg./cm. <sup>2</sup> |
|-------|------------------------|-----------------------------------|
| 1     | 15.5                   | 0.08                              |
| 2     | 20.5                   | 0.13                              |
| 3     | 45.5                   | 0.54                              |
| 4     | 70.5                   | 0.79                              |
| 5     | 95.5                   | 1.17                              |

As a second example of this preferred form of the invention, six cobalt-silicon coated specimens of the alloy were prepared by embedding chemically cleaned and polished specimens of the alloy in a cobaltizing pack of the following mixture:

15 percent by weight of cobalt powder,  
6 percent by weight of NH<sub>4</sub>Cl powder,  
79 percent by weight of Al<sub>2</sub>O<sub>3</sub> powder.

The packs, contained in covered steel cans, were then subjected to thermal treatment in an argon atmosphere at a temperature of about 1800° F. for about 5 hours. During this cobaltizing treatment, the packs were rotated at 1 revolution per minute.

The previously cobaltized alloy substrates were then embedded in a siliconizing pack of the following mixture:

17 percent by weight silicon powder,  
3 percent by weight NaF powder,  
80 percent by weight Al<sub>2</sub>O<sub>3</sub> powder.

These packs, contained in graphite containers, were then subjected to thermal exposure in an argon atmosphere at a temperature of about 2000° F. for about 12 hours. During siliconizing, the pack was rotated at 1 revolution per minute.

The specimens of this example exhibited a cobalt-silicon coating structure substantially identical to that of the previous example. In accordance with the invention, these specimens were then subjected to a preoxidation treatment to deplete the low-melting CoSi<sub>2</sub> component of the cobalt-silicon coating and to improve thereby the maximum-temperature capability of the coating. These specimens were preoxidized at 2200° F. for 10, 25, and 50 hours, two of the specimens being subjected to each respective time. Subsequent to preoxidation treatment, each specimen was oxidation tested at 2400° F. The results of these tests are summarized in Table 7 below. It is significant that no coating failures occurred in any of the specimens during the 2400° F. oxidation test period.

TABLE 7

| Preoxidation Time at 2,200° F., hr. | Weight Gain (mg./cm. <sup>2</sup> ) at 2,200° F. | Weight Gain (mg./cm. <sup>2</sup> ) 100 hr. (8 cycles) at 2,400° F. | Total Weight Gain (mg./cm. <sup>2</sup> ) at 2,200° and 2,400° F. |
|-------------------------------------|--------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------|
| 10                                  | 0.69                                             | 3.64                                                                | 4.33                                                              |
| 10                                  | 0.03                                             | 2.80                                                                | 2.83                                                              |
| 25                                  | 0.77                                             | 3.03                                                                | 3.80                                                              |
| 25                                  | 1.49                                             | 3.91                                                                | 5.40                                                              |
| 50                                  | 1.75                                             | 3.96                                                                | 5.71                                                              |
| 50                                  | 0.85                                             | 1.66                                                                | 2.51                                                              |

FIG. 3 is a photomicrograph enlarged 500 times of a specimen or example of a preferred form of cobalt-silicon coating on the Alloy that was initially prepared in a manner identical to that used to prepare the foregoing example. FIG. 3 shows the coating as it appeared after preoxidation treatment comprising cyclic (8 cycles) oxidation of the specimen for 100 hours at about 2300° F. As shown in FIG. 3, the surface layer or outer zone consists essentially of a complex oxide. Underneath the oxide is a zone consisting essentially of a CoSi matrix with MSi<sub>2</sub> particles dispersed therein, where M represents about the proportionate ingredients as they occur in the substrate. The innermost layer or zone of the coating comprises subsilicides of the substrate diffused in the alloy base metal.

From the foregoing it is thus established that a preferred coating of the cobalt-silicon type can be created by preoxidizing a previously deposited coating that includes both CoSi<sub>2</sub> and CoSi. Preferably, the CoSi layer comprises either a dispersed phase in a matrix of a disilicide of the substrate or a continuous phase forming a matrix for a dispersed disilicide of the substrate. There may also be included, in a preferred form of the coatings of this invention, a layer or zone beneath the CoSi consisting essentially of a disilicide of the substrate. Such a coating system gives excellent results in providing oxidation resistance for columbium and its alloys at temperatures up to at least about 2400° F., whereas cobalt-silicon coatings containing CoSi<sub>2</sub> and which have not been preoxidized, may be expected to fail at temperatures above 2300° F.

In accordance with the invention, any deleterious effects that might be expected to result from the thermal expansion mismatch that exists between CoSi and the

alloy are avoided. Data illustrative of the mismatch are set forth in Table 8 below:

TABLE 8.—MEAN LINEAR THERMAL EXPANSION COEFFICIENTS FOR CoSi AND THE ALLOY

| Temp.<br>Range,<br>° F. | Mean Linear Thermal<br>Expansion Coefficient,<br>in./in. $\times 10^6$ per ° F. |       | Temp.<br>Range,<br>° F. | Mean Linear Thermal<br>Expansion Coefficient,<br>in./in. $\times 10^6$ per ° F. |       |
|-------------------------|---------------------------------------------------------------------------------|-------|-------------------------|---------------------------------------------------------------------------------|-------|
|                         | CoSi                                                                            | Alloy |                         | CoSi                                                                            | Alloy |
| 68-200-----             | 5.5                                                                             | 3.75  | 68-1,400----            | 6.7                                                                             | 4.0   |
| 68-400-----             | 5.7                                                                             | 3.70  | 68-1,600----            | 6.9                                                                             | 4.1   |
| 68-600-----             | 5.8                                                                             | 3.80  | 68-1,800----            | 7.1                                                                             | 4.2   |
| 68-800-----             | 6.0                                                                             | 3.80  | 68-2,000----            | 7.3                                                                             | 4.3   |
| 68-1,000-----           | 6.2                                                                             | 3.90  | 68-2,200----            | 7.4                                                                             | 4.4   |
| 68-1,200-----           | 6.5                                                                             | 3.9   | 68-2,300----            | 7.5                                                                             | 4.5   |

In accordance with the teachings of this invention, when CoSi essentially forms the outer exposed surface layer or zone of the coating, an intermediate layer or zone comprising a disilicide of the substrate exists beneath the CoSi surface layer zone, although the disilicide of the substrate also may be intermixed with the CoSi to an appreciable extent adjacent the CoSi zone. The mean linear thermal expansion coefficient of the disilicides of typical columbium base substrates of this invention inherently lie somewhere between the mean linear thermal expansion coefficients for CoSi and the alloy. Since the intermediate disilicide layer or zone also possesses an intermediate thermal expansion coefficient, it serves, in accordance with the invention, as a thermal expansion buffer or cushion and prevents the thermal mismatch between CoSi and typical columbium base substrates from causing thermal defecting of the coating. This invention thus provides a coating system consisting essentially of an  $MSi_2$  (where M represents about the proportionate ingredients as they occur in the substrate) layer or zone beneath a CoSi surface layer or zone that results in achieving a desirably graded thermal expansion match between the substrate and the CoSi surface layer or zone.

In yet another test, specially shaped bars of the alloy were coated with a cobalt-silicon coating by embedding chemically cleaned and polished bars of the alloy in cobaltizing packs of the following mixture:

15 percent by weight cobalt powder,  
6 percent by weight of  $NH_4Cl$ ,  
79 percent by weight of  $Al_2O_3$  powder.

The packs, contained in covered steel cans, were then subjected to thermal treatment in an argon atmosphere at a temperature of about 1700° F. for about 12 hours. During this cobaltizing treatment, the packs were rotated at 1 revolution per minute.

The previously cobaltized alloy bars were then embedded in a siliconizing pack of the following mixture:

17 percent by weight silicon powder,  
3 percent by weight NaF powder,  
80 percent by weight  $Al_2O_3$  powder.

These packs, contained in graphite containers, were then subjected to thermal exposure in an argon atmosphere at a temperature of about 2000° F. for about 12 hours. During siliconizing, the pack was rotated at 1 revolution per minute.

The coating consisted essentially of an outer zone of CoSi and an inner zone of products of diffusion between the alloy substrate and outer coating zone. This specimen was subjected to a dynamic gas erosion test, where the gas flame simulated the combustion products of a jet engine. During this test, which lasted 100 hours at a temperature of 2200° F. and included several thermal cycles from 2200° F. to room temperature, the coating appeared to completely protect the alloy substrate from oxidation.

The novel coatings of this invention for columbium and columbium base alloy substrates achieve an important,

new and useful result. They possess distinct and unique advantages over the usual types of intermetallic protective coatings such as  $CbSi_2$  or  $CbAl_3$ . 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)  $CoSi_2$  and CoSi compounds, which comprise the desirable ingredients in the cobalt-silicon coatings of this invention, either singly or in combination, exhibit excellent oxidation resistance at temperatures up to at least about 2200° F. (with combinations of CoSi and  $CoSi_2$  being reliably protective at temperatures up to at least about 2300° F. and for CoSi alone, up to about 2400° F.) and are superior to the existing coating materials, typified, for example, by  $CbSi_2$  and  $CbAl_3$ .

(2) When compared with existing coating materials, such as  $CbSi_2$ :

- Coatings containing  $CoSi_2$  as an essential ingredient display markedly improved behavior during oxidation at temperatures up to at least about 2200° F.;
- Coatings containing  $CoSi_2$  and CoSi as essential ingredients exhibit markedly improved behavior during oxidation at temperatures up to at least about 2300° F.;
- Coatings containing CoSi as an essential ingredient display markedly improved behavior during oxidation at temperatures up to at least about 2400° F.;
- Coatings containing as essential ingredients a surface exposed layer or zone of CoSi and an intermediate layer or zone of  $MSi_2$ , where M represents about the proportionate ingredients as they occur in the substrate, display markedly improved behavior during oxidation at temperatures up to at least about 2400° F.;
- Coatings containing as essential ingredients  $CoSi_2$ , CoSi, and  $MSi_2$ , where M represents about the proportionate ingredients as they occur in the substrate, display markedly improved behavior during oxidation at temperatures up to at least about 2300° F.;
- Specifically, coatings having: (i) a CoSi outer layer or zone, either with or without  $MSi_2$ , where M represents about the proportionate ingredients dispersed in the CoSi; (ii) an  $MSi_2$  layer or zone under the CoSi zone; and (iii) a diffusion zone comprising subsilicides of the substrate under the  $MSi_2$  zone, constitute a particularly preferred and outstanding form of this invention and display markedly improved behavior during oxidation at temperatures up to at least about 2400° F.;
- Preferably, each of the foregoing coatings when deposited over the substrate includes an intermediate layer or zone beneath the outer exposed layer or zone consisting essentially of a disilicide of the substrate.

(3) The cobalt-silicon coatings of this invention are highly resistant to low temperature (about 1300° F.) rapid oxidation failure, or the pest phenomenon, that is characteristic of typical unimproved or unmodified intermetallic coatings and the coatings of this invention retain this resistance even after pronounced exposure to high temperature environments, thereby exhibiting excellent thermal stability. In contrast, even some of the improved and modified silicide and aluminate coatings quickly fail when subjected to even mild thermal cycling between low and high temperatures.

(4) The cobalt-silicon coatings of this invention display excellent resistance to local defect failure.

(5) In a preferred form, the cobalt-silicon coatings of this invention consist essentially of a CoSi surface layer or zone with an intermediate layer or subsurface zone beneath the CoSi (and sometimes intermixed with the CoSi in its outer portions) comprising a disilicide of the substrate. Such coatings, primarily because of the intermediate zone containing a disilicide of the substrate, exhibit excellent thermal cyclic failure resistance and provide a desirably graded thermal expansion match, with

progressively increasing thermal expansion coefficients from the columbium base substrate through the disilicide of the substrate to the CoSi surface layer or outermost zone.

(6) The coatings of the present invention possess substantial resistance to the erosive action of a high-velocity gas stream, and thus are useful in dynamic environments.

(7) The coatings of the present invention are relatively insensitive to the process by which they are applied to columbium base substrates and are also relatively insensitive to substrate geometry effects; they thus represent a great step forward in improved oxidation resistant behavior over existing coatings, typified by columbium disilicides and trialuminides.

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, the article having a defect, oxidation, and thermal-cyclic-failure resistant surface zone consisting essentially of at least one compound selected from the group consisting of CoSi, CoSi<sub>2</sub>, and mixtures thereof.

2. 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, the article having a thermal-cyclic-failure, defect, and oxidation resistant surface zone consisting essentially of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi, and mixtures thereof, and a subzone beneath the surface zone consisting essentially of at least one composition selected from the group consisting of CoSi, a disilicide of the metal core, mixtures thereof, and subsilicides of the metal core.

3. The invention as defined in claim 1, in which the surface zone consists essentially of CoSi<sub>2</sub>.

4. The invention as defined in claim 1, in which the surface zone consists essentially of CoSi.

5. The invention as defined in claim 1, in which the surface zone consists essentially of a mixture of CoSi<sub>2</sub> and CoSi.

6. The invention as defined in claim 2, in which the surface zone consists essentially of CoSi and the subzone consists essentially of a mixture of CoSi and a disilicide of the metal core.

7. The invention as defined in claim 2, in which the surface zone consists essentially of CoSi<sub>2</sub> and the subzone consists essentially of CoSi.

8. The invention as defined in claim 2, in which the surface zone consists essentially of a mixture of CoSi<sub>2</sub> and CoSi and the sublayer consists essentially of a silicide of the metal core.

9. A coated metal body comprising a substrate selected from the group consisting of columbium and its alloys and having a protective coating at least on that part of the substrate that is exposed to attack by oxygen and high temperatures, the coating consisting of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof, the coating being oxidation resistant, thermal-cyclic-failure resistant, and defect resistant at high temperatures.

10. A coated metal body comprising a substrate selected from the group consisting of columbium and its alloys and having a protective coating at least on that part of the substrate that is exposed to attack by oxygen at high temperatures, the coating containing a surface

zone consisting essentially of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof, the coating also containing a subzone consisting essentially of at least one compound selected from the group consisting of CoSi, a silicide of the substrate, and mixtures thereof, the coating being oxidation resistant, thermal-cyclic-failure resistant, and defect resistant at high temperatures.

11. As an article of manufacture, a refractory metal body, comprising a substrate selected from the group consisting of columbium and columbium base alloys and having an exterior exposed layer composed predominately of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof, the body being characterized by a good stress-rupture strength at high temperatures, resistance to thermal-cyclic-failure, and resistance to oxidation at temperatures up to at least about 2200° F.

12. A coated metal body having good stress-rupture strength at high temperatures, good oxidation resistance at high temperatures, and resistance to cyclic fatigue failure which comprises a substrate selected from the group consisting of columbium and alloys thereof, and a coating comprising cobalt and silicon wherein substantially all of the cobalt is stoichiometrically combined with the silicon to form at least one compound selected from the group consisting of CoSi and CoSi<sub>2</sub>.

13. The coated metal body according to claim 12, in which excess silicon is present over that required to combine stoichiometrically with the cobalt, the excess silicon being combined with the substrate in the form of at least one compound selected from the group consisting of a disilicide of the substrate and subsilicides of the substrate.

14. The process of coating a fabricated base metal which process comprises surrounding a base metal selected from the group consisting of columbium and alloys thereof with a powdered pack of a finely ground source of cobalt and a small amount of a volatilizable ammonium halide salt as active ingredients and an inert filler, heating the base metal and powdered pack for a time period sufficient to cause volatilization of the ammonium halide salt and to produce deposition of elemental cobalt on the surface of the base metal, then surrounding the cobaltized base metal with a powdered pack of a finely ground source of silicon and a small amount of a volatilizable halide salt as active ingredients and an inert filler, heating the base metal for a time period sufficient to cause volatilization of the halogen in the halide salt and to effect the creation of an exterior surface layer on the base metal composed predominantly of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof.

15. The process of treating a metal from the group consisting of columbium and alloys thereof to render the surface of the metal resistant to oxidation at high temperatures, that includes, heating the metal to a temperature of from about 1400° to 2200° F. in a nonoxidizing atmosphere and in surface contact with a powdered mixture of cobalt, an ammonium halide, and an inert refractory material, and subsequently heating the metal to a temperature of at least about 2000° F. in a nonoxidizing atmosphere with a surface of the metal in contact with a powdered mixture of silicon, an inorganic halide and an inert refractory material to form thereby a protective surface coating on the metal consisting essentially of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof.

16. A method of producing a high temperature oxidation resistant, thermal-cyclic-failure resistant, defect insensitive coating surface layer on a metal article formed of a substrate selected from the group consisting of columbium and columbium base alloys, the coating surface layer consisting essentially of at least one compound selected from the group consisting of CoSi<sub>2</sub>, CoSi and mixtures thereof; the method comprising the steps of:

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enclosing the article in a cobaltizing pack of powdered material containing a source of cobalt and a small amount of a volatilizable ammonium halide salt as essential active ingredients and an inert filler, heating the article in the pack to a temperature higher than that causing volatilization of the ammonium halide salt, and maintaining this temperature for a discrete interval of time to effect the deposition of cobalt onto the surface of the article, then enclosing the cobaltized article in a siliconizing pack of powdered material containing a source of silicon and a small amount of a volatilizable halogen generating substance as essential ingredients and an inert filler, heating the article in the pack to a temperature higher than that causing volatilization of the substance to effect the creation of an exterior surface layer composed predominantly of at least one compound selected from the group consisting of  $\text{CoSi}_2$ ,  $\text{CoSi}$  and mixtures thereof.

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17. The method as defined in claim 16, in which the metal article during the cobaltizing step is heated in the pack to a temperature of from about  $1400^\circ$  to  $2200^\circ$  F.

18. The method as defined in claim 16, in which the metal article is heated in the siliconizing pack to a temperature at least about  $2000^\circ$  F. for from about  $\frac{1}{2}$  to 50 hours.

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