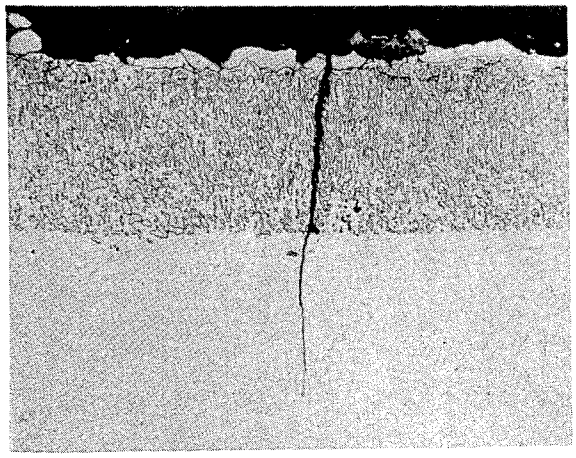
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COATINGS FOR COLUMBIUM BASE ALLOYS

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STRUCTURE OF A 1:2 Mn:Si RATIO COATING

500X MAGNIFICATION

Inventor

ELIHU F. BRADLEY
EDWIN S. BARTLETT
HORACE R. OGDEN
ROBERT I. JAFFEE

By

Irons, Birch, Swindler & McKie

Attorney

United States Patent Office

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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 modified silicide coatings for columbium and its alloys in which the coatings are created by 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 modified silicide coatings on columbium base materials to produce a protective layer over the base metal 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 2200° 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 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 fabricable material, and 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 incompatability 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-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 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 as compared with molybdenum base alloys are the columbium 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 2200° 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 base 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 (i.e., columbium, molybdenum, tantalum, and tungsten) from oxidation at temperatures up to about 3000° F. In general, the more effective of these intermetallic coatings are further classified as silicides, aluminides and beryllides. 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 sprayings, 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 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, NH_4I, NH_4Cl, and the like), and an inert filler material (e.g., Al_2O_3, SiO_2, 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, $CbAl_3$ (aluminide), or $CbSi_2$ (silicide), and the like.

The more favorable coatings (aluminides, silicides, beryllides) for columbium 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 toward 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° F.) temperatures (this characteristic of silicide coatings is sometimes termed "the silicide pest phenomenon") and at high (about 2000° F. or higher) temperatures. Modification of silicide coatings is highly desirable to impart to them sufficient longevity to give them a utility that 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° 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 at least about 2200° F., and that will achieve a modified silicide coating that is highly resistant to failure at localized sites.

Further objects of this invention are to provide a coating for columbium and columbium base alloys 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 columbium base alloys (1) a coating that is self-healing, i.e., in the presence of a major defect that exposes the alloy substrate to corrosive environment, the surrounding coating exhibits the ability to generate additional coating that will grow over the defect, thus reestablishing a protective barrier between the alloy substrate and its corrosive environment; (2) a coating that in nominal thicknesses of 2 to 5 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° F.; (3) a coating that exhibits excellent resistance to thermal shock failure; (4) a coating that displays excellent defect insensitivity at both higher and lower temperatures than glass-forming temperature for the coating; (5) a coating that demonstrates self-healing capabilities at temperatures above the glass-forming temperature; and (6) a coating that achieves significant resistance to high velocity gas erosion.

Still further objects to this invention are to provide a method for coating columbium and columbium base alloys with a modified columbium silicide 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.

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 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 columbium base alloys, the article having a thermal shock failure resistance, defect insensitive, self-healing surface layer or coating consisting essentially of a mixture of manganese silicide and a silicide of the metal core. The coating may have a manganese to silicon ratio by weight of from about 3:1 to 1:5, but gives particularly outstanding results when the manganese to silicon ratio by weight is from about 1:1 to 1:3, and in its most preferred form the manganese to silicon ratio of the coating by weight is found to be about 1:1.5.

More particularly described and in a preferred embodiment, the coating of this invention comprises: a mixed phase surface zone or region consisting essentially of a mixture of manganese silicide and a disilicide of the substrate or metal core and a subzone or region essentially underneath the surface zone and consisting essentially of a disilicide 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 alloys thereof and having an exterior exposed layer composed predominantly of a mixture of manganese silicide and a silicide of the metal body, the body being characterized by a good stress-rupture strength at high temperatures and a high resistance to oxidation at temperatures up to at least about 2200° F.

The invention also includes within its scope 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 core of metal selected from the group consisting of columbium and its alloys, the body having a thermal shock failure resistant, defect insensitive, self-healing oxidation resistant coating, the coating comprising: a mixed phase surface zone consisting essentially of a mixture of manganese silicide and a disilicide of the metal core, an intermediate region essentially beneath the surface zone consisting essentially of a disilicide of the metal core, and a diffusion zone adjacent the metal core consisting essentially of at least one subsilicide of the metal core. The coating in this form of the invention may have a manganese to silicon ratio by weight of from about 2:1 to 1:5, but gives particularly outstanding results when the manganese to silicon ratio by weight is from about 1:1 to 1:3, and in its most preferred form the manganese to silicon ratio of the coating by weight is about 1:1.5.

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 comprises depositing a surface coating on a metal substrate, the substrate being a metal selected from a group consisting of columbium and alloys thereof, and

the coating consisting essentially of manganese silicide and a silicide of the metal 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 alloys thereof with a powdered pack of a finely ground sources of manganese and a small amount of a volatilizable 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 halogen in the halide salt and to produce deposition of elemental manganese on the surface of the base metal, then surrounding the manganized 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 manganese silicide and a silicide of the base metal.

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

Quite unexpectedly, if silicide coatings for columbium and its structural alloys are modified with manganese in accordance with this invention, the deleterious effects of both the "low" temperature silicide pest phenomenon and the "high" temperature rapid oxidation mechanism are essentially overcome. The manganese-modified silicide 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° F. These coatings possess distinctly superior oxidation resistance and superior defect insensitivity up to at least about 2200° F. and overcome and counteract the tendency of unmodified or manganese-free silicide coatings on columbium substrates to fail at critical temperatures of about 1300° F. and from about 2000° to about 2200° F.

In the embodiments forming the examples of this invention, two different substrates were used for the manganese modified silicide coatings. These substrates are:

(1) Unalloyed columbium, ¼-inch-diameter rod.
(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," ⅛ to ¼-inch-diameter rod.

Other columbium-base alloys could have been used equally well as substrates to illustrate the new and desirable performance of the manganese-modified silicide coatings for columbium and its alloys described in this specification.

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.

Manganese-modified silicide coatings were applied to these substrates 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 manganizing pack of the following mixture:

37 percent by weight of manganese powder
3 percent by weight of NaCl powder
60 percent by weight of Al_2O_3 powder.

The packs, contained in covered steel cans, were then subjected to various thermal treatments in an argon atmosphere at temperatures ranging from 1800° F. to 2200° F. for times from about 1 hour to about 10 hours as required to deposit a desired amount of manganese. Successful deposition of manganese can also be achieved in accordance with the invention at temperatures ranging from 1400° F. to 2400° F. During this treatment, manganese reacted with the substrate to form the compound M Mn_2 at the surface (where M represents about the proportionate ingredients as they occur in the substrate). For example, the manganese-rich coating over columbium was $CbMn_2$, and over the Alloy was essentially

$$(Cb\text{-}20Ta\text{-}15W\text{-}5Mo)Mn_2$$

The second cycle comprised embedding the previously manganized Cb or Alloy substrates in a siliconizing pack of the following mixture, expressed in weight per gram:

17 percent silicon powder
3 percent NaF powder
80 percent Al_2O_3 powder.

These packs, contained in covered steel cans, were then subjected to various thermal exposures in an argon atmosphere at temperatures from about 2000° to about 2400° F. for times ranging from about ½ hour to about 4 hours as required to form the desired thickness of manganese modified silicide coating (thicknesses between 3 and 6 mils were achieved). During this treatment, the silicon-rich atmosphere within the pack reacted first with the M Mn_2 compound to generate about equal volumes of mixed phases based on MnSi and MSi_2 structures. After depletion of the original M Mn_2 phase, silicon reacted with the substrate, forming additional MSi_2 phase to achieve the desired total coating thickness. An alternative siliconizing procedure was to pack previously manganized substrates in a siliconizing pack of the following weight percent mixture:

5 percent silicon powder
3 percent NaF powder
92 percent Al_2O_3 powder.

Graphite cups were used as containers for this pack mix. Siliconizing kinetics using the lean mixture in graphite cups were about identical to those using the rich mixture in steel cans when siliconizing was conducted at 2200° F. Still another procedure, utilizing the rich (17 percent silicon) pack in graphite containers resulted in more rapid rates of deposition.

The procedures described above are representative of only one method by which manganese-modified silicide coatings can be deposited upon columbium-base substrates. The superior performance of the coating abides in the composition and structure of the coating, and is not restricted to coatings deposited by the pack cementation process.

Representative examples of manganese-modified silicide coatings forming embodiments of this invention are set forth in Table 1, which also reports the coating conditions utilized in achieving these representative coatings. In accordance with the invention, it has been discovered that the most significant distinguishing characteristic of these coatings is the ratio of specific weight gain during manganizing to the specific weight gain during siliconizing. This ratio, which controls the chemical composition and, to a large extent, the structure of the manganese-modified silicide coatings, is set forth in the last column of Table 1.

TABLE 1.—EXAMPLES OF MANGANESE-MODIFIED SILICIDE COATINGS

Example	Substrate	Manganizing			Siliconizing			Coating thickness, mil [a]	Ratio, Mn:Si [b]
		Temp., ° F.	Time, hr.	Specific weight gain, mg./cm.²	Temp., ° F.	Time, hr.	Specific weight gain, mg./cm.²		
1	Alloy [c]	2,200	10.5	20.2	2,200	0.65	[d] 6.7	4.0	3:1
2	do	2,200	3.1	13.6	2,200	1.17	[d] 14.2	4.2	1:1
3	Columbium	2,200	2	11.2	2,200	4	[e] 17.1	4.2	1:1.5
4	Alloy	2,200	2	12.4	2,200	4	[e] 19.0	4.7	1:1.5
5	do	2,200	2	15.8	2,200	4	[e] 31.0	7.0	1:2
6	do	2,200	2.2	11.5	2,200	2.5	[f] 33.2	6.7	1:3
7	do	1,900	7	7.9	2,200	2.5	[f] 39.2	7.0	1:5
8	do	1,900	2.5	4.6	2,200	2.5	[f] 36.5	6.1	1:8

[a] Calculated on total weight-gain basis. 6.7 mg./cm.²—1-mil coating approximately.
[b] Ratio of specific weight gain in manganizing:specific weight gain in siliconizing.
[c] Alloy substrate is Cb-20Ta-15W-5Mo (weight percent additions).
[d] Siliconized in graphite cups using lean pack mixture.
[e] Siliconized in steel cans using rich pack mixture.
[f] Siliconized in graphite cups using rich pack mixture.

The effects of this Mn:Si weight ratio upon coating chemistry and structure can best be understood by using one of the reference examples. The drawing shows the structure of a manganese-modified silicide coating applied to the Alloy substrate by manganizing for 2 hours at about 2200° F. followed by siliconizing in the rich pack mixture contained in a steel can for 4 hours at about 2200° F. The resulting Mn:Si ratio was 1:2. Chemical analysis of this type of structure, performed by electron beam microprobe techniques, showed the subsilicide region to be consistent with an M_5Si_3 phase. Analysis of the disilicide zone was consistent with an MSi_2 phase. In each case, "M" represents proportionate amounts of columbium, tantalum, tungsten, and molybdenum (i.e., Cb-20Ta-15W-5Mo). Neither phase contained more than 2 to 3 percent by weight of manganese. The outer, mixed-phase region consisted of the gray-etching MnSi phase, containing about 15 percent by weight of substrate elements (Cb, Ta, W, Mo), and the manganese deficient MSi_2 phase (the white matrix of this region, as shown in the drawing).

In accordance with the invention, the coating structure may be controlled by controlling the ratio by weight of Mn to Si in the manganese-modified silicide coatings. For example, with higher Mn:Si ratios (1:1.5, 1:1, 1.5:1) the mixed-phase region is predominant, and with lower ratios (1:3, 1:5, 1:8) the disilicide region is predominant. Similarly, the structure of the mixed-phase region may be controlled by adjustment of variables of the coating process itself. For example, by increasing the rate of deposition during siliconizing, such as, by using a rich pack in graphite cups, the MnSi phase can be made to predominate, and the proportionate quantity of MSi_2 phase in the mixed phase region will then be less than that shown in the drawing.

In accordance with the invention, and as an unexpected new and beneficial result, the manganese-modified silicide coatings of this invention form a manganese silicate glass when exposed to temperatures in excess of about 1900° F.; it is believed that the greatly improved oxidation resistance achieved by the coatings of this invention is in part due to the formation of this glass. Also unexpectedly and beneficially, the manganese-modified silicide coatings of this invention begin to vitrify at about 1900° F., which is well below the minimum glass formation temperature that has previously been reliably reported to be 2200° F. for the $MnO\text{-}SiO_2$ system. E. M. Levine, H. F. McMurdie, and F. P. Hall, Phase Diagrams for Ceramists, American Chemical Society, Columbus, Ohio, 1956. Even at temperatures below those at which vitrification occurs upon oxidation, however, the manganese-modified silicide coatings of this invention are distinctly superior in oxidation resistance to unmodified silicide coatings for columbium base substrates.

To evaluate the protection afforded to columbium base substrates by the manganese-modified silicide coatings of this invention, cyclic oxidation tests were conducted at temperatures of 1000°, 1300°, 1600°, 1900°, 2200°, and 2500° F. in ambient air (no forced air flow). During testing, specimens, supported on refractory oxide boats, were inserted in an electrically heated muffle furnace preset at the desired temperature. Specimens were removed periodically from the furnace and cooled to room temperature for visual examination and weighing, after which they were returned to the furnace for additional oxidation exposure. Time intervals for cyclic exposures were as shown in Table 2 below:

TABLE 2

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

Testing at each temperature was arbitrarily discontinued after a total of 100 hours oxidation without failure was achieved.

By oxidizing examples of the manganese-modified silicide coatings of this invention at various Mn:Si ratios under the program described above (Table 2) at 1300° and 2200° F. temperatures (representative of a "low" and "high" oxidation temperature), it was possible to establish the optimum or preferred Mn:Si ratios for achieving the new and useful results of the invention. The results of these runs are set forth in Table 3. As shown in Table 3, the manganese-free silicide coatings over columbium and the Alloy (Examples 10 and 11) failed within 20 hours at 1300° F. by gross powdering or severe localized defecting of the coating. During 2200° F. oxidation, the manganese-free, nominally 5-mil-thick silicide coatings oxidized severely, and protected the substrate for only 75–100 hours. In these examples, the kinetics of oxidation follow a linear rate law, that is, the products of oxidation do not appreciably restrict further oxidation.

TABLE 3.—OXIDATION TESTS OF MANGANESE-MODIFIED SILICIDE COATINGS OVER UNALLOYED COLUMBIUM AND Cb-20Ta-15W-5Mo ALLOY

Example	Substrate	Mn:Si ratio	1,300° F. oxidation		2,200° F. oxidation	
			Duration of test, hr.	Cumulative weight change, mg./cm.²	Duration of test, hr.	Cumulative weight change, mg./cm.²
1	Alloy [a]	3:1	100	0.7	75	[b] 4.7
2	do	1:1	100	0.3	100	[b] 3.4
3	Columbium	1:1.5	100	[c] −7.4	100	5.5
4	Alloy	1:1.5	100	−0.1	100	3.7
6	do	1.3	100	0.5	100	5.8
7	do	1:5	100	1.1	100	[d] 12.6
8	do	1:8	20	[e]	50	[d] 16.0
9	Columbium	1:1	No test	No test	100	[b] 1.4
10	Alloy	[f] 0	20	[e]	100	[d] 33.4
11	Columbium	[f] 0	20	[e]	75	[d] 30.4

[a] Alloy is Cb-20Ta-15W-5Mo.
[b] Excess glass absorbed by support. Actual weight change higher.
[c] One large piece of coating spalled. Overall performance unimpaired.
[d] Gross uniform oxidation of coating.
[e] Gross failure by local defect or powdering of coating.
[f] Manganese-free silicide coating.

The behavior of various manganese-modified silicide coatings on columbium and alloys thereof is summarized below:

(1) In coatings containing only about 1 part by weight of manganese to 8 parts by weight silicon, the manganese modification has little effect. At both temperatures (1300° and 2200° F.) the coatings behave as though almost no modification had been achieved. (Example 8.)

(2) Coatings containing at least 1 part of manganese to 5 parts of silicon consistently protect the substrates for at least 100 hours at 1300° F. (Examples 1, 2, 3, 4, 6, 7.)

(3) A coating containing 1 part of manganese to 5 parts of silicon oxidizes at a lower rate than manganese-free silicide coatings for 50 to 75 hours at 2200° F., but thereafter oxidizes rapidly in a manner characteristic of manganese-free silicide coatings. The limited amount of glass-forming phase, MnSi, is not sufficient to be protective for more than about 75 hours. (Example 7.) However, even this amount of protection represents an appreciable advantage over manganese-free silicide coatings.

(4) A coating containing about 1 part of manganese to 3 parts of silicon is fully protective for 100 hours at 2200° F. However, after the 100-hour-test the surface of the specimen exhibits little glaze, and it is apparent that life of the coating beyond 100 hours would be limited. (Example 6.)

(5) Coatings containing about 1 part of manganese to 1½ parts of silicon are protective for 100 hours at 2200° F. Weight gains during the first 4½ hours are high (about 3½ mg./cm.²) as the protective glass is formed. During the last 95 hours of a 100 hour test at 2200° F., weight gains are very low, about 2 mg./cm.², showing the excellent protection of the glass oxidation product. After completing 100 hours at 2200° F., appreciable quantities of MnSi phase are still present in the microstructures of the coatings. These coatings thus exhibit a capability for protection substantially greater than 100 hours at 2200° F. (Examples 3 and 4.)

(6) Coatings containing about equal weights of manganese and silicon are also fully protective for 100 hours at 2200° F. However, the amount of glass formed may be excessive; during the test it ran off the specimens and was absorbed by the supporting refractory oxide boats. Weight changes reported in Table 3 are thus unrealistically low. The excessive amount of glass formed in general is undesirable, as it is not required for adequate protection. Despite excessive glass formation, however, appreciable quantities of MnSi phase are still present in the microstructures of the coatings after 100 hours oxidation at 2200° F. These coatings thus indicate a capability for protection of substantially greater than 100 hours at 2200° F. (Examples 2 and 9.)

(7) A coating containing 3 parts of manganese to 1 part of silicon exhibits the MSi_2 phase only in the mixed phase region, and although it endures for 75 hours before failure, it is not adequately protective at 2200° F. An excessive amount of glass is formed. (Example 1.)

Accordingly, within its scope this invention includes manganese-modified silicide coatings for columbium-base materials, in which the Mn:Si ratios by weight are from about 3:1 to 1:5. Such coatings are able to protect columbium alloy substrates for periods of time greater than 100 hours both at temperatures of about 1300°, at which the disilicide pest phenomenon occurs, and at temperatures of about 2000° to about 2200° F., at which a rapid oxidation mechanism occurs. They are thus greatly superior to unmodified or manganese-free silicide coatings. Performance of coatings in the examples forming embodiments of this invention discloses that intermediate ratios of from about 1:1 to 1:3 are particularly outstanding and that a ratio of about 1:1.5 is preferred.

The oxidation behavior of typical manganese-modified silicide coatings for columbium-base materials has been further clarified by oxidation of nominal 5-mil thick, 1:1.5 Mn:Si ratio coatings at temperatures of 1000°, 1600°, 1900°, and 2500° F. Test results on such coatings at the named temperatures are summarized in Table 4. Table 4

TABLE 4.—CHARACTERIZATION OF THE BEHAVIOR OF 5-MIL-THICK, 1:1.5 Mn-Si RATIO COATINGS OVER COLUMBIUM AND Cb-20Ta-15W-5Mo ALLOY DURING CYCLIC OXIDATION IN AIR AT VARIOUS TEMPERATURES

Example	Substrate	Oxidation Temp., ° F.	Duration of Test, hr.	Cumulative Weight Change, mg./cm.²	Remarks
4A	Alloy	1,000	100	0.2	
3A	Columbium	1,000	100	0.7	
4B	Alloy	1,300	100	−0.6	Minor oxide spalling.
3B	Columbium	1,300	100	−7.4	Piece of coating spalled.
4C	Alloy	1,600	100	1.3	
3C	Columbium	1,600	100	1.8	
4D	Alloy	1,900	100	3.8	
3D	Columbium	1,900	100	4.6	
4E	Alloy	2,200	100	6.6	
3E	Columbium	2,200	100	5.0	
4F	Alloy	2,500	75	4.8	Failed at local defect in 100 hours.
3F	Columbium	2,500	75		Complete oxidation.

also includes the results of 1300° and 2200° F. testing reported previously. At 1000°, 1600°, and 1900° F., oxidation was mild and the coatings easily protected the substrates for 100 hours. Oxidation resistance of the manganese-modified coating over columbium-base materials at these temperatures was about the same as that exhibited by unmodified or manganese-free silicide coatings, which also perform well at these temperatures. At 2500° F., the manganese-modified silicide coatings investigated were limited to a capability of protecting the columbium-base substrates for about 50–75 hours. Essentially the same behavior was exhibited by unmodified or manganese-free silicide coatings at this temperature.

After the tests described above had shown the superior performance of the manganese-modified silicide coated columbium-base materials during cyclic oxidation, tests were conducted on additional examples or embodiments of the invention to demonstrate resistance of the coated systems to thermal shock, intentional defects, and high velocity gaseous erosion, as well as their ability to achieve self-healing of intentionally introduced defects. (Defects to a depth of at least 5 and 6 mils in both columbium and the Alloy respectively were healed within 3 hours at 2200° F., and those to a depth of at least 9 mils in the Alloy were healed after an additional exposure of 17 hours including 1 cycle at 1½ hours and 1 cycle at 15½ hours.) For most of these tests, rod specimens of both unalloyed columbium and the Alloy were coated in a manner described previously to achieve nominal 5-mil-thick manganese-modified silicide coatings with nominal Mn:Si ratios between 1:1.6 and 1:1.2.

For thermal shock testing, two coated Alloy specimens were placed in a cavity in a long stabilized zirconia boat. The boat was then wrapped with 18-gage Chromel A wire with a pitch of about ⅛ inch to retain the specimens in the boat, but not to restrict access of the specimens to the environment. Specimens were free to slide within the confines of the boat. Before thermal shock testing, specimens were preoxidized for 1 hour at 2200° F. to form the characteristic glass. To test the resistance of the coated systems to thermal shock, the boat was placed in an electric fired furnace at 2200° F. In about 1 minute the assembly was about at that temperature, but was allowed an additional 1 to 4 minutes for thermal stabilization (or a total of 2 to 5 minutes heating at 2200° F.). The boat containing the specimens was then removed from the furnace and the specimens were immediately (about 1 second elapsed time) given a blast of air issuing from a 1/16-inch orifice in an 80 p.s.i. air line. The rate of cooling was governed by the distance between the orifice and the specimens, and was measured as shown in Table 5 below:

TABLE 5

Distance, in.	Cooling Rate, degrees/sec.
8	65
2	200

Thus, for the lower cooling rate, 15 seconds were required to cool from 2200° F. to a black heat, whereas at the higher rate, only 5 seconds were required The entire assembly was cooled to about room temperature for each cycle.

A record of the thermal shock testing of these specimens and the results are given in Table 6. Specifically, it

TABLE 6.—HISTORY OF THERMAL SHOCK TESTING OF MANGANESE-MODIFIED SILICIDE COATING ON A COLUMBIUM-BASE ALLOY

Operation	Observation
13 cycles, low cooling rate	No change in appearance.
7 cycles, high cooling rate	Do.
15 min. soak at 2,200° F	Do.
20 cycles, high cooling rate	Do.
95 hr. soak at 2,200° F	No effects from thermal shock.
15 cycles, high cooling rate (one specimen arbitrarily removed for metallography; tests continued on other specimen).	No change in appearance.
24 hr. soak at 2,200° F., plus water quench.	Do.
23 hr. soak at 2,200° F., plus normal air cool.	Slight spalling of oxide at edge.

Total time at 2,200° F.—153 hr.
Cycles, low cooling rate—13.
Cycles, high cooling rate—42.
Cycles, water quench—1.
Total thermal shock cycles—56.

was shown that the manganese-modified silicide coating over a representative columbium alloy can sustain repeated quenching from 2200° F. to about room temperature without failure. Furthermore, as some of the thermal shock cycles were conducted after about 100 hours oxidation exposure, the thermal stability of the coating regarding thermal shock resistance is excellent. Microstructurally, the coatings showed no detrimental effects that could be attributed to thermal shock.

Defects were intentionally introduced in several manganese-modified silicide coated columbium and Alloy specimens by two methods:

(1) Coated specimens were indented with a diamond pyramid hardness indenter (Vickers) with loads up to 50 kilograms. Maximum depths of the indentations were 4.9 mils in the case of coated columbium, and 2.4 mils in the case of the coated Alloy (reflect-

ing primarily the greater hardness of the Alloy substrate compared with unalloyed columbium). Although no fracture of the coating as a result of Vickers indentation was apparent macroscopically, metallographic examination showed complete fracture paths through the coatings beneath the indentations, providing potential free access of air to the substrate.

(2) Coated specimens were notched with a file to depths as shown in Table 7 below:

TABLE 7

Notch	Depth in Mils		Remarks
	Coated Columbium	Coated Alloy	
1	3	3	Did not penetrate coating.
2	5	6	Barely penetrated coating.
3	8	9	Appreciable substrate exposed.
4	16	16	Gross defect.

Examples of Vickers indented specimens were exposed to oxidation at 1600° F. (below the glass forming temperature) and 2200° F. (within the glass forming temperature range) for times of 75 hours and 100 hours, respectively, with no failures observed. Good defect insensitivity was thus demonstrated for the manganese-modified silicide coatings over columbium-base materials. File-notched specimens were oxidized at 2200° F. to assess the self-healing capability of the glass coating in stagnant air. After the first (1½ hours) oxidation cycle, substrate oxidation was observed at all three notches where the coating had been penetrated (Notches 2, 3, and 4). During the second cycle (1½ hours), self-healing occurred at Notch 2 of specimens of both systems (coated columbium and Alloy), but not at the two deeper notches. No additional change was noted during the third (1½ hours) cycle. However, during the fourth cycle (15½ hours), self-healing occurred at Notch 3 of the coated Alloy restricting further substrate oxidation at this site. This phenomenon was not observed, however, on the coated columbium example. This test thus demonstrates the self-healing capability of the manganese-modified silicide coating over columbium-base substrates at temperatures at which the glass is formed upon oxidation.

A special shaped specimen was machined from the Alloy and coated with a 3-mil thick, 1:1 Mn:Si ratio manganese-modified silicide coating. This specimen was then subjected to a special gas erosion test designed to simulate the gas chemistry and velocity conditions existing in the turbine of a turbojet engine operating at 2200° F. The test consisted of 8 cyclic exposures to the high velocity gas, each of 5-hours duration, for a total test time of 40 hours. Through 35 hours accumulated time, the surface of the specimen exhibited the normal glassy appearance, but on the last cycle, the appearance indicated depletion of the MnSi glass-forming plase. This was confirmed by metallographic examination, which showed none of the protective glass-forming, mixed phase region remaining.

This erosion test showed that although high velocity gas significantly increases the rate of depletion of the protective glass-forming mixed phase region compared with a static atmosphere, protection attributable to the manganese modification is still appreciable.

In accordance with the invention, it has thus been shown that manganese-modified silicide coatings for columbium-base alloys exhibit greatly superior oxidation resistance to unmodified or manganese-free silicide coatings over the same substrates. Silicide coatings containing weights of manganese from about 3 times to ⅓ the weight of silicon present exhibit this superiority. Coatings containing weights of manganese from about equal to, to ⅓ the weight of silicon present are particularly outstanding, while coatings containing a ratio by weight of 1:1.5, manganese to silicon, are most preferred. It has been further demonstrated that such manganese-modified silicide coatings for columbium and its alloys exhibit excellent resistance to thermal shock failure, excellent defect insensitivity at temperatures both higher and lower than the glass-forming temperature, at least moderate self-healing capabilities at temperatures above the glass-forming temperatures, and significant resistance to high velocity gas erosion.

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 thermal shock failure resistant, defect insensitive, self-healing oxidation resistant surface layer consisting essentially of a mixture of manganese silicide and a silicide of the metal core.

2. The invention as defined in claim 1, in which the surface layer has a manganese to silicon ratio by weight of from about 3:1 to 1:5.

3. The invention defined in claim 1, in which the surface layer has a manganese to silicon ratio by weight from about 1:1 to 1:3.

4. The invention as defined in claim 1, in which the surface layer has a manganese to silicon ratio by weight of about 1:1.5.

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, the article having a thermal shock failure resistant, defect insensitive, self-healing oxidation resistant coating comprising: a surface zone consisting essentially of a mixture of manganese silicide and a disilicide of the metal core and a subzone essentially beneath the surface zone and consisting essentially of a disilicide of the metal core.

6. A coated metal body comprising a substrate selected from the group consisting of columbium and columbium base 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 mixture of manganese silicide and a silicide of the metal body and being oxidation resistant, thermal shock failure resistant, defect insensitive and self-healing at high temperatures.

7. The invention as defined in claim 6, in which the coating has a manganese to silicon ratio by weight of from about 3:1 to 1:5.

8. The invention as defined in claim 6, in which the coating has a manganese to silicon ratio by weight from about 1:1 to 1:3.

9. The invention as defined in claim 6, in which the coating has a manganese to silicon ratio by weight of about 1:1.5.

10. A coated metal body comprising a substrate selected from the group consisting of columbium and columbium base 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 comprising: a surface zone containing a mixture of manganese silicide and a disilicide of the metal body and a subzone essen-

tially beneath the surface zone and containing a disilicide of the metal body, the coating being oxidation resistant, thermal shock failure resistant, defect insensitive, and self-healing 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 predominantly of a mixture of manganese silicide and a silicide of the metal body, the body being characterized by a good stress-rupture strength at high temperatures and a high resistance to oxidation at temperatures up to at least about 2200° F.

12. The invention as defined in claim **11**, in which the exterior exposed layer has a manganese to silicon ratio by weight of from about 3:1 to 1:5.

13. The invention as defined in claim **11**, in which exterior exposed layer has a manganese to silicon ratio by weight from about 1:1 to 1:3.

14. The invention as defined in claim **11**, in which the exterior exposed layer has a manganese to silicon ratio by weight of about 1:1.5.

15. 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 core of metal selected from the group consisting of columbium and alloys thereof, the body having a thermal shock failure resistant, defect insensitive, self-healing oxidation resistant coating, the coating comprising: a mixed phase surface zone consisting essentially of a mixture of manganese silicide and a disilicide of the metal core, an intermediate region beneath the surface zone consisting essentially of a disilicide of the metal core, and a diffusion zone adjacent the metal core consisting essentially of at least one subsilicide of the metal core.

16. The invention as defined in claim **15**, in which the coating has a manganese to silicon ratio by weight of from about 2:1 to 1:5.

17. The invention as defined in claim **15**, in which the coating has a manganese to silicon ratio by weight of from about 1:1 to 1:3.

18. The invention as defined in claim **15**, in which the coating has a manganese to silicon ratio by weight of about 1:1.5.

19. 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 manganese and a small amount of a volatilizable 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 halogen in the halide salt and to produce deposition of elemental manganese on the surface of the base metal, then surrounding the manganized 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 manganese silicide and a silicide of the base metal.

20. 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 between from about 1400° to 2400° F. in a non-oxidizing atmosphere and in surface contact with a powdered mixture of manganese, an inorganic halide, and an inert refractory material, and subsequently heating the metal to a temperature of from about 2000° to about 2400° F. in a non-oxidizing atmosphere with the 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 manganese silicide and a silicide of the base metal.

21. A method of producing a high temperature oxidation resistant, thermal shock failure resistant, defect insensitive, self-healing 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 a mixture of manganese silicide and a silicide of the metal substrate; the method comprising the steps of: enclosing the article in a manganizing pack of powdered material containing a source of manganese and a small amount of a volatilizable halogen generating substance as essential active ingredients and an inert filler, heating the article in the pack to a temperature higher than that causing volatilization of the halogen substance, and maintaining this temperature for a discrete interval of time to effect the deposition of manganese onto the surface of the article, then enclosing the manganized 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 active ingredients and an inert filler, 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 a mixture of manganese silicide and a silicide of the substrate.

22. The method as defined in claim **21**, in which the metal article during the manganizing step is heated in the pack to a temperature of from about 1400° F. to 2400° F.

23. The method as defined in claim **21**, in which the metal article is heated in the siliconizing pack to a temperature of from about 2000° to about 2400° F. for from about one-half hour to about 4 hours.

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ALFRED L. LEAVITT, *Primary Examiner.*

A. GOLIAN, *Assistant Examiner.*