

April 13, 1971

L. A. FRIEDRICH ET AL

3,574,572

COATINGS FOR HIGH-TEMPERATURE ALLOYS

Filed April 14, 1964

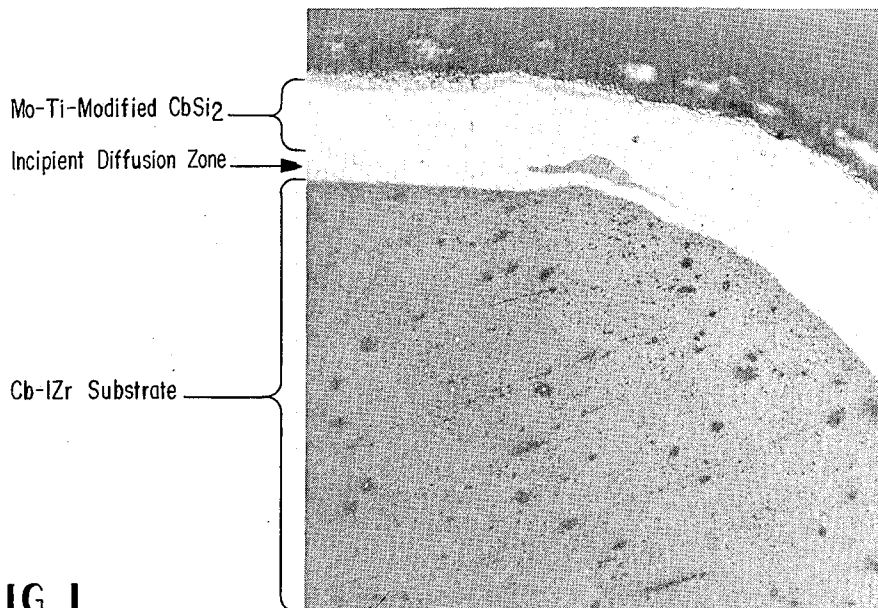


FIG. 1.

Mo-Ti-Modified Columbium Silicide Coating on Cb-IZr Substrate
(As-Coated Condition)

500X

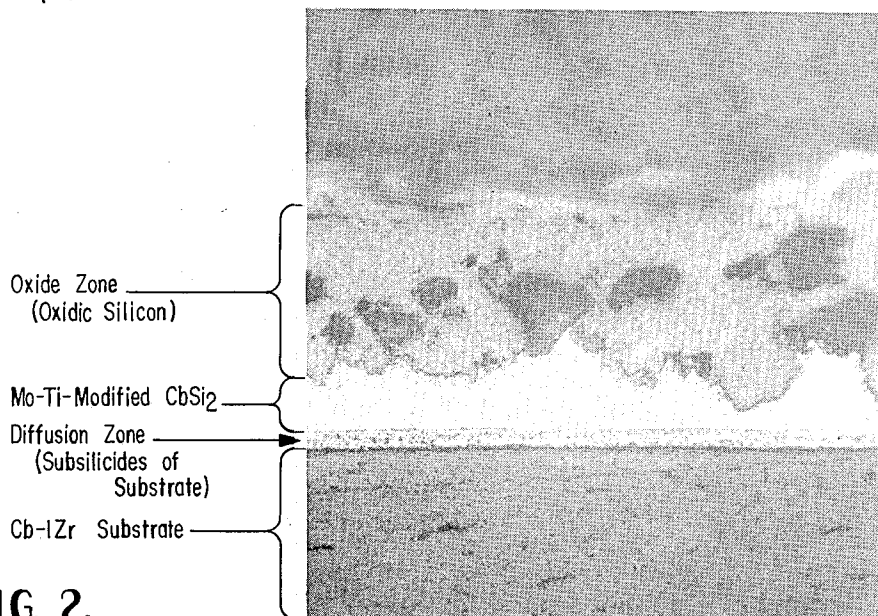


FIG. 2.

Mo-Ti-Modified Columbium Silicide Coating on Cb-IZr Substrate
After Exposure in Static Air for 100 Hours at 2000° F

500X

Inventors.

LEONARD A. FRIEDRICH
EMANUEL C. HIRAKIS

334
Drew, Birch, Swindler, and McKie
Attorneys.

1

3,574,572

COATINGS FOR HIGH-TEMPERATURE ALLOYS
Leonard A. Friedrich, West Hartford, and Emanuel C.
Hirakis, Mansfield Center, Conn., assignors to United
Aircraft Corporation, East Hartford, Conn.
Filed Apr. 14, 1964, Ser. No. 360,177
Int. Cl. B23p 3/00

U.S. Cl. 29—198

17 Claims

This invention relates to novel coatings for columbium and columbium base alloys that will protect the base metal or alloy from oxidation at high temperatures and to a method for creating such coatings.

More particularly, this invention relates to molybdenum-titanium-modified columbium silicide coatings for columbium and its alloys in which the coatings are created by methods, such as vapor deposition, electrophoretic deposition, and the like. The invention also particularly relates to a method for obtaining vapor deposition of such molybdenum-titanium-modified silicide coatings on columbium base materials to produce a protective layer or zone over such materials providing an oxidation-resistant coating at high temperatures, such as, for example, temperatures up to at least 2000° F. in air and even higher for short exposure times.

During exposure to oxidation at elevated temperatures an oxide coat is formed on the outer or exposed zone of the coating and at diffusing temperatures an inner diffusion zone is created between the molybdenum-titanium-modified silicide and the substrate. Upon exposure the structure of the coating is thus to this extent altered. The oxide coat and diffusion zone once formed are stable in structure and function as part of the protective coating system.

For many years it has been generally known that the high-temperature strength properties of metals are closely related to their melting points. In general, metals having high melting points thus are capable of forming alloys having high strength at high temperatures.

The need for structural materials for service at temperatures in excess of those obtainable with existing structural materials has stimulated interest in the metals having the highest melting points, or the refractory metals, particularly, chromium, columbium, tantalum, molybdenum and tungsten.

Molybdenum was once considered the chief prospect as a base metal in alloys for such usage. At the high-temperature service conditions needed, however, molybdenum not only oxidizes, but the molybdenum oxide formed, is volatile, once the oxidation reaction begins it tends to progress rapidly until molybdenum is consumed at a catastrophic rate.

As an alloy base material for high temperature service, columbium offers more 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 (4474° F.) and its low neutron-capture cross-section. Columbium is, therefore, potentially useful as a structural material for containment vessels for high-temperature liquid metals.

Further, columbium is inherently a soft, ductile, readily fabricable material, and although it becomes too weak for practical structural uses at temperatures much above 1200° F., it readily can be strengthened for use at much higher temperatures by alloying with various metals, and particularly by alloying with the refractory metals. Columbium is also a highly reactive metal in that it dissolves large quantities of oxygen and nitrogen, upon exposure to atmospheres containing even small amounts of these elements at relatively modest temperatures.

2

Although columbium oxidizes rapidly at high temperatures, in contrast to molybdenum which oxidizes catastrophically, columbium oxide does not volatilize. It is thus potentially possible to prevent oxygen attack on columbium by coating the metal, and if premature localized coating failure should occur, to restrict such failure and oxygen attack to the localized site. Further advantages offered by columbium 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.

The history of columbium alloy technology has, however, demonstrated the incompatibility of achieving oxidation resistance and high-temperature strength through alloying alone. Since the major uses for columbium base alloys are as structural components in high-temperature applications, it is apparent that useful classes of high-temperature columbium alloys will require protective coatings in their normal high-temperature oxidizing environments.

A particularly important potential area of use for columbium base alloys as dictated by economic and technological factors is in structural materials designed for exposure to oxidizing environments at temperatures up to about 2000° F. (a temperature that clearly establishes utility for these alloys). Concomitantly, such alloys must be able to resist mechanical stresses for appreciable periods of time at these high temperatures.

About 500° F. is the maximum operating temperature to which columbium base alloys may be subjected for extended times in the uncoated condition without serious oxidation, and at temperatures much above 500° F. the oxidation problem becomes acute.

The art has previously recognized certain oxidation resistant intermetallic coatings as exhibiting 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 silicides, aluminides and beryllides of the base metal.

In considering coatings for the refractory metals, both coatings and substrate materials importantly affect the performance of the coated systems. For example, a silicide coating over columbium may perform quite differently from one over molybdenum with the difference in performance attributable to the substrate rather than to the coating type. As an additional confirmation of the importance of the substrate, some species of coatings that are reliably protective over other of the refractory metals are ineffective over columbium and are susceptible to failure on columbium at high temperatures. Coating and substrate must thus be evaluated and treated as an integrated system. Success with a particular coating on a particular base metal does not mean the coating will be successful when used over a different base metal.

Several methods, such as, flame or plasma torch spraying, slurry application techniques, electrophoretic deposition, hot pressure bonding or vapor deposition, have been used for applying intermetallic coatings to columbium base alloys. A vapor deposition process that can be used advantageously to achieve 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, (1) the metal to be reacted with or deposited upon the object to be coated (e.g., silicon, aluminum, beryllium), (2) an activator or energizer (usually a halide salt, such as NaCl, KF, NH₄I, NH₄Cl, and the like), and (3) an inert filler material (e.g., Al₂O₃, SiO₂, BeO, MgO, and the like).

This mixture, held in a suitable container (such as, a steel box, graphite boat or refractory oxide crucible), is then heated to the desired coating temperature in a pre-

scribed 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 columbium, the major proportions of which may be compounds, such as, CbAl_3 , 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° F.) or at "high" temperatures (about 2000° F. and above). Perhaps the most serious deficiency of existing coatings for columbium, however, is their propensity for failing at localized sites.

Silicide coatings on columbium and its structural alloys are more stable than aluminides and have a better thermal expansion match with the substrate than beryllides which have such a severe thermal expansion mismatch that it prohibits their use. With columbium the silicides are thus of primary interest.

Silicide coatings on structural columbium alloy substrates, however, are prone to consumption by rapid oxidation at "low" (about 1300° F.) temperatures. This characteristic of silicide coatings is sometimes termed "the silicide pest phenomenon." Modification of silicide coatings is thus highly desirable to impart sufficient longevity and reliability to give to them a utility they do not normally possess.

Copending application Ser. No. 360,176, filed Apr. 14, 1964, discloses a titanium-modified columbium silicide coating composition that effectively protects columbium-base alloys from oxidation in static air at temperatures up to at least 1800° F. for times in excess of 5000 hours.

Coatings of this composition are particularly effective in overcoming the silicide pest phenomenon, characterized by consumption of columbium silicide coatings by rapid oxidation at temperatures of about 1300° F., and also in overcoming the rapid oxidation of columbium silicide coatings at higher temperatures of about 2000° F. Such coatings are, however, subject to the disadvantage of remaining brittle up to high use temperatures making them subject to failure from mechanical shocks while in use. And in some embodiments they may even retain brittle characteristics up to temperatures as high as 2000° F.

Accordingly, it is a primary object of this invention to provide a new and improved titanium-modified columbium silicide coating composition that is co-modified by the addition of molybdenum. The molybdenum additive significantly improves the plasticity of the titanium-modified columbium silicide coating and imparts plasticity and ductility to the coating at use temperatures and at temperatures appreciably lower than those at which plasticity and ductility can be achieved with straight Ti-modified columbium silicide coatings.

The increased plasticity and ductility achieved by the addition of molybdenum to the Ti-modified columbium silicide coating also significantly improves the reliability of the coating by increasing its resistance to mechanical stress, mechanical shock and local defect failure, particularly where such failure is induced by brittleness of the coating.

Another object of this invention is to provide a molybdenum-titanium-modified columbium silicide coating for columbium and its 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, and formation of defects. They are also diffusionally stable, well-bonded to the substrate and resistant to spalling.

Other objects of this invention are to provide for columbium and its alloys:

(1) A coating that in nominal thicknesses of 1½ to 3 mils is capable of providing protection to exposure in

static air for time in excess of 5000 hours at temperatures up to at least about 1800° F.

(2) A coating that exhibits excellent resistance to thermal and mechanical shock failure; and

(3) A coating that displays excellent resistance to the formation of defects at both higher and lower temperatures of exposure.

A still further object of this invention is to provide a method for coating columbium and its alloys with a molybdenum-titanium-modified columbium silicide composition coating by a vapor deposition (pack-cementation) process that achieves substantial uniformity of the coating and yields 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.

As set forth in the description of the invention and in the claims it will be understood that the term "use temperature" refers to those temperatures at which the coatings of the invention are usefully protective over columbium base substrates. So defined, "use temperature" encompasses elevated temperatures up to about 2300° F. Although the useful life of the coating falls off rapidly at temperatures above 2000° F., it has been established that at 1800° F. the coatings have a useful life of greater than 5000 hours.

The term "diffusing temperature" refers to those temperatures at which a diffusion zone forms by interdiffusion between the coating and substrate taking place at an appreciable rate. A preferred "diffusing temperature" for the coatings of this invention is 1800° F. At this temperature interdiffusion proceeds at an advantageous speed until a distinct diffusion zone is formed, and it is unnecessary and uneconomical to use a higher temperature. Once the diffusion zone is formed it essentially stabilizes, and loss of the coating through diffusion into the substrate is prevented. Diffusing temperatures of from 1700 to 1900° F. are efficacious, and even higher temperatures up to 2300° F. would achieve the desired result, but at 2300° F., if the diffusion is accomplished in an oxidizing atmosphere, the life of the coated article would be short.

Exposure to the diffusing temperature is normally effected during actual use of the coated articles and not as a separate step, and is thus simultaneous with exposure to an oxidizing environment at elevated temperatures. At about 1800° F. diffusion begins with exposure and continues until the structure of the coating system becomes essentially stabilized after about 25 hours of exposure.

To achieve the foregoing objects and in accordance with its purpose, this invention includes an article of manufacture having good resistance to oxidation in air at elevated temperatures, which article comprises a core of metal selected from the group consisting of columbium and columbium base alloys, the article having a defect, spalling, and thermal and mechanical shock failure resistant surface region or coating consisting essentially of columbium silicide (preferably CbSi_2) modified by titanium and molybdenum, the surface layer being characterized by measurable ductility at use temperatures in excess of 1500° F.

The invention further comprehends an article of manufacture having good resistance to oxidation in air at elevated temperatures, which article comprises a core of metal selected from the group consisting of columbium and columbium base alloys, the article having a defect, spalling, and thermal and mechanical shock failure resistant shell or coating, the shell or coating consisting essentially of a surface zone of columbium silicides (preferably CbSi_2) modified by titanium and molybdenum and,

after exposure to a diffusing temperature in a nonoxidizing atmosphere, a diffusion zone or subzone beneath the surface zone consisting essentially of subsilicides of the substrate, the shell or coating being characterized by measurable ductility at use temperature in excess of 1500° F.

The invention may also be described as including a new and improved article of manufacture having good resistance to oxidation in air at high temperatures, which article comprises a core of metal selected from the group consisting of columbium and alloys thereof, the article having a thermal and mechanical shock failure resistant, defect resistant, spalling resistant and broad range oxidation-resistant shell or coating, the shell or coating being characterized after exposure to an oxidizing environment at a diffusing temperature effective to create interdiffusion between the coating and metal core, by an exposed layer or surface zone consisting essentially of oxidic silicon (normally SiO_2), an intermediate layer or subzone consisting essentially of columbium silicide (preferably CbSi_2) modified by titanium and molybdenum, and an inner layer of diffusion zone beneath the subzone consisting essentially of subsilicides of the substrate, the shell or coating being characterized by measurable ductility at use temperatures in excess of 1500° F.

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 a defect, spalling, oxidation and thermal and mechanical shock resistant protective coating comprising, after exposure to a diffusing temperature in an oxidizing environment, an exterior exposed layer or zone composed predominantly of oxidic silicon (normally SiO_2), a sublayer or intermediate zone beneath the exterior or exposed layer or zone composed predominantly of columbium silicides (preferably CbSi_2) modified by titanium and molybdenum, and a second sublayer or diffusion zone beneath the first sublayer or intermediate zone composed predominantly of subsilicides of the substrate; the body being characterized by good resistance to oxidation at elevated temperatures, and the protective coating being characterized by measurable ductility at use temperatures in excess of 1500° F.

In accordance with its purpose, this invention includes a method of producing a coated metal article having resistance to oxidation at high temperatures, which method 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 columbium silicide (preferably CbSi_2) modified by titanium and molybdenum and characterized by measurable ductility at use temperatures in excess of 1500° F.

One embodiment of such method includes a 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 silicon, a finely ground source of titanium, a finely ground source of molybdenum, 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 halide salt and to produce a deposition of silicon, titanium and molybdenum on the surface of the base metal thereby effecting the creation of an exterior surface zone or coating on the base metal composed predominantly of columbium silicide (CbSi_2) modified by titanium and molybdenum and characterized by measurable ductility at use temperatures in excess of 1500° F.

Such method may be extended to include the step of exposing a metal article (the exposure normally being effected during actual use), previously coated as described with Mo-Ti-modified columbium silicide, to an oxidizing environment at a diffusing temperature to effect inter-

diffusion between the coating and base metal and the creation of an outer exposed layer or surface zone consisting essentially of oxidic silicon, an intermediate layer or subzone consisting essentially of columbium silicide (preferably CbSi_2) modified by titanium and molybdenum, and an inner layer or diffusion zone beneath the subzone composed predominantly of subsilicides 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 pest phenomenon") and at "high" (about 2000° F.) temperatures. At the latter temperature a rapid oxidation mechanism begins to occur 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 molybdenum-titanium-modified silicide 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 molybdenum-titanium-modified columbium silicide coatings of the present invention have thus proven to be particularly outstanding in their ability to protect columbium and its alloys from oxidation under a wide variety of conditions of use and for substantial periods of time at temperatures up to at least 2000° F. These coatings possess distinctly superior oxidation resistance to unmodified silicide coatings and overcome the tendency of titanium-free silicide coatings on columbium substrates to fail at the critical temperatures of about 1300° F. and 2000° F. and above.

In accordance with this invention, typical substrates, in addition to unalloyed columbium, to which the molybdenum-titanium-modified silicide coatings of this invention have been applied, parts expressed as percentages by weight, are as follows:

ALLOY 1

Columbium	99
Zirconium	1
(Cb-1Zr).	

ALLOY 2

Columbium	95
Titanium	5
(Cb-5Ti).	

ALLOY 3

Columbium	88
Titanium	8
Molybdenum	4
(Cb-8Ti-4Mo).	

ALLOY 4

Columbium	88
Titanium	8
Vanadium	4
(Cb-8Ti-4V).	

ALLOY 5

Columbium	93
Vanadium	5
Aluminum	2
(Cb-5V-2Al).	

ALLOY 6

Columbium	95
Zirconium	5
(Cb-5Zr).	

ALLOY 7

Columbium	78
Titanium	8
Molybdenum	4
Tungsten	10
(Cb-8Ti-4Mo-10W).	

7 ALLOY 8

Columbium -----	94.5
Vanadium -----	5
Chromium -----	0.5
(Cb-5V-0.5Cr).	

ALLOY 9

Columbium -----	87
Vanadium -----	7
Aluminum -----	3
Tungsten -----	3
(Cb-7V-3Al-3W).	

In accordance with this invention, suitable halide salts are as follows:



The preferred halide salt for best results with the present invention is, however, aluminum fluoride (AlF_3).

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 an alloy consisting essentially of Cb-1Zr by weight, hereafter referred to as "the Alloy," was selected as a representative substrate material. Other columbium-base alloys such as those set forth previously could have been used equally well as substrates to illustrate the new and desirable performance of the molybdenum-titanium-modified silicide coatings for columbium base alloys described in this specification.

EXAMPLE 1

Columbium silicide coatings modified by titanium and molybdenum were applied to the Cb-1Zr substrate, or "the Alloy," by utilizing a pack-cementation process, which comprised embedding chemically cleaned specimens to be coated in a pack of the following mixture:

- 11 grams (99 cc.) of Al_2O_3 powder (micron particle size)
- 9 grams of titanium powder (minus 100 mesh)
- 6 grams of molybdenum powder (minus 200 mesh)
- 14 grams of silicon powder (minus 200 mesh)
- 4 grams of AlF_3

The packs, contained in "Inconel" containers, were subjected to purging by argon flowthrough for 2 hours and then to thermal treatments at temperatures ranging from 1800 to 2200° F. and for times from about 4 to 16 hours, with 16 hours at 1800° F. being the preferred thermal treatment.

The thickness of the coating deposited was controlled by the time temperature relationships used. A lower coating temperature is generally preferred for economy of operation, and this is particularly important when the process is scaled up.

In accordance with the invention, during thermal treatment an argon flowthrough was maintained in the pack at atmospheric pressure or slightly above. This flowthrough was equivalent to about 10 cc. of argon per minute through a 500 cc. canister.

When the reaction had proceeded to the extent desired, the canister was removed from the furnace and cooled under a flow of argon.

During this treatment, the silicon titanium, molybdenum and substrate reacted to yield a molybdenum titanium-modified CbSi_2 structure in which titanium and molybdenum were present in relatively small amounts as determined by electron microprobe studies and X-ray diffractions analysis.

8

Although the exact mechanism of the modification or change wrought by Mo and Ti on CbSi_2 in this invention is not known, it is believed that Ti and Mo atoms, respectively, are substituted for Cb atoms to a small but important extent in the CbSi_2 lattice structure.

Even though the amounts of Ti and Mo substitution for Cb in the CbSi_2 are small, such amounts are highly effective. The Ti and Mo modification greatly improves the reliability of CbSi_2 as a coating and significantly increases its plasticity giving the coating a measurable ductility at use temperatures in excess of 1500° F.

Thicknesses of the molybdenum-titanium-modified silicide coating varied from 1½ to 4 mils depending upon specific deposition conditions.

Desired thicknesses of these coatings were from about 1½ to 3 mils, preferably about 2 mils.

The inert filler material is not limited to Al_2O_3 , since almost any refractory oxide filler, such as zirconia or beryllia, also works well.

The coating thus produced was found to protect the alloy for periods in excess of 5000 hours at temperatures up to at least 1800° F. The coating is also protective over the alloy for shorter periods at even higher temperatures up to 2300° F.

Although many of the halide salts will produce the desired results, ammonium fluoride (NH_4F) should not be used, since it tends to cause hydrogen and nitrogen embrittlement of the columbium. Aluminum fluoride (AlF_3) is the preferred salt, and it works especially well because of its high vapor pressure.

EXAMPLE 2

A chemically cleaned specimen of the alloy was embedded in a pack of the following mixture:

- 11 grams (90 cc.) of Al_2O_3 powder (micron particle size)
- 7 grams of titanium powder (minus 100 mesh)
- 8 grams of molybdenum powder (minus 200 mesh)
- 15 grams of silicon powder (minus 200 mesh)
- 4 grams of potassium fluoride (KF)

The pack, contained in an "Inconel" container, was purged for 2 hours with argon, and then subjected to thermal exposure in an argon atmosphere at a temperature of 1800° F. for 16 hours. After exposure, the pack was removed from the furnace and allowed to cool under a flow of argon. The resulting coating was about 3 mils thick and consisted essentially of a molybdenum-titanium-modified CbSi_2 structure in which titanium and molybdenum were present in small amounts. This coating protected the substrate in excess of 5000 hours at 1800° F.

FIG. 1 is a photomicrograph magnified 500 times showing a representative Mo-Ti-modified columbium silicide coating of this invention over the alloy in the as-coated condition. This coating, as is characteristic of the coatings of this invention, is very uniform both in composition and thickness; it is also well-bonded to the substrate and highly resistant to spalling. An incipient diffusion zone is also shown in FIG. 1. This zone was probably created by interdiffusion between the coating and substrate during the latter stages of the pack-cementation process in which the coating was formed.

FIG. 2 is a photomicrograph enlarged 500 times showing the Mo-Ti-modified silicide coating of this invention over the alloy after exposure to an oxidizing environment for 100 hours at 2000° F. As can be seen from the photomicrograph FIG. 2, the basic molybdenum-titanium-modified silicide coating remains essentially unchanged in composition and thickness; however, the diffusion zone between the substrate and the coating has been emphasized and given more definite structure by the additional exposure at a diffusion temperature. The diffusion zone is composed principally of subsilicides of the substrate. Also, during this exposure to an oxidizing environment, a relatively thick layer comprising oxidic sili-

con is formed as the outer or exposed zone of the specimen.

As is characteristic of the coatings of this invention, and in accordance with the invention, the coating shown in FIG. 2 after formation of the diffusion zone has become essentially stabilized. The coating will remain essentially unchanged in the form shown in FIG. 2 for additional thousands of hours of exposure to oxidation in static air at temperatures up to at least 2000° F. Although the mechanism is not clearly understood it appears that after its formation the diffusion zone acts together with the silicide intermediate zone to provide a superior combined coating that acts as a barrier to oxidation and fissuring and provides effective resistance to spalling and thermal and mechanical shock. The size of the diffusion zone in FIG. 2 indicates that once it is formed there is very little loss of the coating through diffusion into the substrate.

In accordance with the invention, the molybdenum-titanium-modified silicide coatings composed essentially of CbSi_2 modified by titanium and molybdenum are created by codeposition of titanium, molybdenum, and silicon in a pack-cementation process as previously described.

The desired coatings can be achieved with a pack mixture in which the weight ratio of metals in the pack mixture is as follows:

From 6 to 10 parts by weight titanium,
From 6 to 12 parts by weight of molybdenum, and
From 12 to 16 parts by weight of silicon.

The preferred composition of the pack mixture is 9 parts of titanium, 6 parts of molybdenum, and 14 parts of silicon.

Still further in accordance with the invention, the hardness of the resulting coating can be expressed as a function of the atomic or weight ratios of metals in the pack composition. As shown in Table 1 below although an atomic ratio of titanium to molybdenum of about 3:1 (weight ratio of 3:2) produces distinctly advantageous results, the general results of the invention can be achieved with atomic ratios of titanium to molybdenum that vary from 1:1 to 10:3 and weight ratios that vary from 1:2 to 5:3.

TABLE 1

Pack metals (by atomic ratio):	Coating hardness— DPH
Silicon -----	1365
TiSi_2 -----	1231
$(\text{Ti}_{0.5}\text{Mo}_{0.5})\text{Si}_2$ -----	849
$(\text{Ti}_{0.75}\text{Mo}_{0.25})\text{Si}_2$ -----	679

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) The molybdenum-titanium-modified silicide coatings of this invention composed essentially of columbium silicide (preferably CbSi_2) modified by titanium and molybdenum exhibit excellent long term oxidation resistance at temperatures up to at least 2000° F., and are superior to the existing coating materials, typified, for example, by CbSi_2 and CbAl_3 . Such coatings are also an improvement upon columbium silicide coatings modified by titanium alone in that the coatings of this invention have conspicuously greater plasticity and measurable ductility at use temperatures making them more resistant to mechanical shock and stress failure at such temperatures.

(2) When compared with existing coating materials, such as CbSi_2 , the molybdenum-titanium-modified silicide coatings of this invention are highly resistant to "the pest phenomenon" or "low" temperature (about 1300° F.) rapid oxidation failure that is characteristic of typical

titanium-free silicide coatings, and the coatings of this invention retain this resistance even after repeated exposure to high-temperature environments, thereby exhibiting excellent thermal stability. In contrast, even some improved and modified silicide and aluminide coatings are prone to fail when subjected to relatively mild thermal cycling between low and high temperatures.

(3) The coatings of this invention impart long term reliability to columbium base structures operating in static air. For example, when used as pipes for liquid metal in power plants or heat exchangers, the protection afforded the columbium substrates by these coatings enables such power plants and exchangers to be operated at higher and more efficient temperatures over longer periods of time.

(4) After treatment at a diffusing temperature, including treatment that may be concomitant with exposure to an oxidizing atmosphere during actual use of a coated article, the coatings of this invention achieve diffusional stability; the diffusion zone created is composed essentially of subsilicides of the substrate between the deposited molybdenum-titanium-modified silicide coating and the substrate and does not change in size. Loss of coating through diffusion into the substrate is prevented.

(5) Although a thermal expansion mismatch exists between the coatings of this invention and typical columbium base substrates, the coatings as-deposited are thin enough so that they take on the characteristics of the substrate and expand and contract with the substrate. There is excellent adherence of the coatings to the substrate and they are thus well-bonded and highly resistant to spalling.

(6) The coatings of this invention are characteristically highly uniform in both composition and thickness, are mechanically stress and shock resistant, and are compatible with columbium base substrates in that they form no low melting phases or volatile compounds.

As used in this specification the expression " CbSi_2 " will be understood to include all those forms of columbium silicide in which the atomic ratio of columbium to silicon is of the order of 1:2. And the expression " SiO_2 " will be understood to include all those forms of oxidic silicon in which the atomic ratio of silicon to oxygen is in the order of 1:2.

The invention in its broader aspect is not limited to the specific details shown and described and 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 which comprises a core of metal selected from the group consisting of columbium and columbium base alloys, the article having a defect, spalling and thermal and mechanical shock failure resistant surface zone that is oxidation resistant at high temperatures, the surface zone consisting essentially of columbium silicides modified by titanium and molybdenum and characterized by measurable ductility at use temperatures in excess of 1500° F.

2. An article having good resistance to oxidation in air at elevated temperatures, which article comprises a core of metal selected from the group consisting of columbium and columbium base alloys, the article having a defect, spalling, and thermal and mechanical shock failure resistant coating consisting essentially of a surface zone of columbium silicide modified by titanium and molybdenum and, after exposure to a diffusing temperature in a nonoxidizing atmosphere, a diffusion zone beneath the surface zone consisting essentially of subsilicides of the metal core, the coating being characterized by measurable ductility at use temperatures in excess of 1500° F.

3. An article of manufacture having good resistance to oxidation in air at high temperatures which comprises

11

a core of metal selected from the group consisting of columbium and alloys thereof, the article having a thermal and mechanical shock failure resistant, defect resistant, spalling resistant, and broad range oxidation-resistant shell, the shell being characterized, after exposure to an oxidizing environment at a diffusing temperature effective to create interdiffusion between the shell and the metal core, by an exposed surface zone consisting essentially of oxidic silicon, and intermediate zone consisting essentially of columbium silicide modified by titanium and molybdenum, and a diffusion zone beneath the intermediate zone consisting essentially of subsilicides of the metal core, the shell being characterized by measurable ductility at use temperatures in excess of 1500° F.

4. 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 zone composed predominantly, after exposure to a diffusing temperature in an oxidizing environment, of oxidic silicon, an intermediate zone beneath the exposed zone composed predominantly of columbium silicide modified by titanium and molybdenum, and a diffusion zone beneath the intermediate zone composed predominantly of subsilicates of the substrate; the body being characterized by good resistance to oxidation at temperatures up to at least 2000° F.

5. A coated metal body comprising a substrate selected from the group consisting of columbium and its alloys and having a protective shell at least on that part of the substrate that is exposed to attack by oxygen at high temperatures, the coating consisting essentially of columbium silicide modified by titanium and molybdenum, the shell being oxidation-resistant, thermal and mechanical shock failure resistant, spalling resistant, and defect resistant at high temperatures.

6. A coated metal body comprising a substrate selected from the group consisting of columbium and its alloys and having a protective shell at least on that part of the substrate that is exposed to attack by oxygen at high temperatures, the shell, after exposure to an oxidizing environment at a diffusing temperature, having a surface zone consisting essentially of oxidic silicon, an intermediate zone beneath the surface zone consisting essentially of columbium silicide modified by titanium and molybdenum, and a diffusion zone beneath the intermediate zone consisting essentially of subsilicides of the substrate; the shell being oxidation resistant, thermal and mechanical shock failure resistant, spalling resistant, and defect resistant at high temperatures and being characterized by measurable ductility at use temperatures in excess of 1500° F.

7. 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 silicon, a finely ground source of titanium, a finely ground source of molybdenum, 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 halide salt and to produce codeposition of silicon, titanium and molybdenum on the surface of the base metal, thereby effecting the creation of an exterior surface zone on the base metal consisting essentially of columbium silicide modified by titanium and molybdenum and characterized by measurable ductility at use temperatures in excess of 1500° F.

8. The invention as defined in claim 7, in which the process includes the further step of exposing the previously coated base metal to an oxidizing environment at a diffusing temperature to effect the creation of an outer

12

exposed surface zone consisting essentially of oxidic silicon, an intermediate zone beneath the surface zone consisting essentially of columbium silicide modified by titanium and molybdenum, and a diffusion zone beneath the intermediate zone composed predominantly of subsilicides of the base metal.

9. The process of claim 7, in which the halide salt is AlF_3 .

10. The process of claim 7, in which the ratio by weight of titanium to molybdenum in the powdered pack is about 3 to 2.

11. The process of claim 7, in which the ratio by weight of titanium to molybdenum in the powdered pack is from 1:2 to 5:3.

12. 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 1800° F. to 2200° F. in a nonoxidizing atmosphere and in surface contact with a powdered mixture of silicon, titanium, molybdenum, a halide salt and an inert refractory material, to form thereby a protective surface shell on the metal consisting essentially of columbium silicide modified by titanium and molybdenum and characterized by measurable ductility at use temperatures in excess of 1500° F.

13. The invention as defined in claim 12, in which the halide salt is AlF_3 .

14. The invention as defined in claim 12, in which the metal is heated from 4 to 16 hours.

15. The invention as defined in claim 12, in which the heating step is carried out for 16 hours at 1800° F.

16. A method of producing a high-temperature oxidation resistant, thermal and mechanical shock failure resistant, spalling resistant, and defect resistant surface shell on a metal article formed of a substrate selected from the group consisting of columbium and columbium base alloys, the coating surface shell consisting essentially of columbium silicide modified by titanium and molybdenum, the method comprising the steps of: enclosing the article in a siliconizing-titanizing-molybdenizing pack of powdered material containing a source of silicon, a source of titanium, a source of molybdenum and a small amount of volatilizable 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 halide salt, and maintaining this temperature for a discrete interval of time to effect the deposition of silicon, titanium and molybdenum onto the surface of the article, thereby creating an exterior surface shell consisting essentially of columbium silicide modified by titanium and molybdenum.

17. The method of claim 14, that includes the further step of exposing the metal article with its protective shell to an oxidizing environment at a diffusing temperature to effect the creation of a surface zone on the shell consisting essentially of oxidic silicon, an intermediate zone beneath the surface zone consisting essentially of columbium silicide modified by titanium and molybdenum, and a diffusion zone beneath the intermediate zone composed predominantly of subsilicides of the substrate.

References Cited

UNITED STATES PATENTS

65	2,665,475	1/1954	Campbell et al.	29—198
	3,086,886	4/1963	Kieffer et al.	117—107

LELAND A. SEBASTIAN, Primary Examiner

U.S. Cl. X.R.

29—194, 195; 117—107, 127, 131, 135.1