METHODS FOR PRODUCING MULTILAYERED, OXIDATION-RESISTANT STRUCTURES ON SUBSTRATES

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Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 193 days.

Patent No.: US 8,097,303 B2
Date of Patent: Jan. 17, 2012

Abstract

Methods for producing multilayered, oxidation-resistant structures on substrates are provided. The methods comprise depositing silicon dioxide on a substrate comprising molybdenum and boron and annealing the silicon dioxide at a temperature and for a time sufficient to form a coating comprising a borosilicate scale on the substrate.

10 Claims, 12 Drawing Sheets
FIG. 1
FIG. 2

(a) Epoxy
MoSi₂
Substrate

5 µm

Intensity (A.U.)

2 theta

(b) MoSi₂

(c)

0 20 40 60 80 100

0 20 40 60 80 100

400 0

0 20 40 60 80 100
FIG. 3

(b) 200 nm

(c) 20 nm
FIG. 4

![Graph showing exposure time vs. thickness for uncoated and silicide coated samples. The graph indicates a significant increase in thickness over time for the uncoated sample compared to the silicide coated one.](image)
FIG. 6

Sprayed TiO$_2$

In-situ SiO$_2$

40 μm
FIG. 8
FIG. 9

[Graph showing X-ray diffraction data with peaks at 20°, 35°, and 40°. Peaks are labeled as MoO2 and Mo.]
FIG. 10

(a)

(b)

MoO$_2$ Precipitate

Borosilicate
FIG. 11
FIG. 12

(a) [Image of microstructure with labels 1, 2, 3]

(b) [Image of microstructure with labels 1, 2, 3]

2µm

EHT = 10.00 kV
WD = 3 mm
Signal A = SE
Photo No. = 1

40µm

4µm
METHODS FOR PRODUCING MULTILAYERED, OXIDATION-RESISTANT STRUCTURES ON SUBSTRATES

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of and claims priority to U.S. Ser. No. 11/299,427, filed Dec. 12, 2005, now U.S. Pat. No. 7,560,138, which is a divisional of and claims priority to U.S. Ser. No. 10/428,336, filed May 2, 2003, now U.S. Pat. No. 7,005,191, which claims priority to U.S. Provisional Application No. 60/467,076, filed May 1, 2003, the entire disclosures of which are incorporated herein by reference in their entireties and for all purposes as if fully set forth herein.

STATEMENT OF GOVERNMENT INTERESTS

This invention was made with United States government support awarded by the Navy/ONR under grant number N00014-02-1-004 and Air Force/AFOSR under grant number F33615-98-C-7801. The United States government has certain rights in this invention.

FIELD OF THE INVENTION

The invention relates to oxidation resistant coatings for transition metal substrates and transition metal alloy substrates and method for making the same.

BACKGROUND OF THE INVENTION

For structural materials that are intended for high temperature application, it is essential that the material offer some level of inherent oxidation resistance in order to avoid catastrophic failure during use. Nickel based alloys, or superalloys, represent one class of material that is commonly used for high temperature applications, such as turbine components. These nickel based alloys have been found to exhibit good chemical and physical properties under high temperature, stress, and pressure conditions, such as those encountered during turbine operation. However, as larger planes with faster take-off speeds have developed, a need has arisen for turbine materials that can withstand greater temperatures.

Multiphase intermetallic materials composed of molybdenum silicides are one alternative to the nickel based superalloys. These multiphase alloys may include either boron or chromium in addition to molybdenum and silicon and have the potential to withstand much higher operating temperatures than the nickel based superalloys. Although the chemical and physical properties of these molybdenum silicide alloys are promising, oxidation of these materials at high temperatures remains a significant problem in their development for use in high temperature applications. At high temperatures (above about 800°C) these materials naturally form protective oxide coatings that hinder continued oxidation of the underlying material. However, this coating is insufficient to completely halt the oxidation process and over time the reaction of oxygen with molybdenum consumes the alloy.

SUMMARY OF THE INVENTION

The present invention provides oxidation resistant coatings for transition metal substrates and transition metal alloy substrates. The coatings may be multilayer, multiphase coatings or contiguous multiphase coatings having a compositional gradient extending from the substrate outward. The coatings form a protective layer that prevents the substrate from oxidizing which results in a weakening of the substrate through dissolution or disintegration, particularly at high temperatures. The use of the coatings allows the substrates to be used in very high temperature applications where high strength is required. Because the coatings provided by the present invention are actually integrated into the underlying substrate they are resistant to cracking and peeling under the hot/cold cycles that are typically experienced by transition metals and transition metal alloys under actual operating conditions.

The coatings contain multiple phases, including phases of molybdenum, borosilicates, molybdenum borosilicides, and molybdenum silicides. Specific phases may include α-Mo (known as the BCC phase), Mo5SiB2 (known as the T2 phase), Mo5Si3 with a small amount of boron (less than 5 atomic %) (denoted Mo5Si3(B) and known as the T1 phase), Mo5Si (known as the A15 phase), and Mo5Si3 (known as the C11 phase).

A broad variety of substrates may benefit from the coatings of the present invention. The coating may be grown on any substrate having phase constituents of molybdenum (e.g. BCC), molybdenum silicides (e.g. T2 or A15 or C11 or combinations thereof), and molybdenum borosilicides (e.g. T1) at the surface of the substrate. In some instances, the substrate may itself be an alloy comprising molybdenum, silicon, and boron (denoted a Mo-Si-B alloy). In other cases the substrate will have a surface that has been enriched with molybdenum, silicon, and/or boron to produce a substrate surface having a Mo-Si-B alloy character. In either case, the surface of the substrate is desirably rich in molybdenum.

In addition to molybdenum silicides, borosilicates, and borosilicides, the coatings may include other compounds wherein the chemical composition of at least one of the phase constituents within the coating is all or partly replaced by other transition metals, other metalloids, simple metals or combinations thereof. For example, the coating may be a Mo-Ti-Cr-Si-B coating wherein a portion of the molybdenum in the coating has been chemically substituted with Ti and/or Cr in the BCC and T2 phases. Alternatively, the coating may be a Mo-Si-Al coating wherein Al is substituted for a portion of the Si in the Mo5Si3 (A15) phase.

Two and three phase Mo-Si-B alloys are specific examples of molybdenum silicide alloys that benefit from the coatings of the present invention. A first aspect of the present invention provides a multilayered, multiphase, oxidation resistant coating comprising molybdenum, silicon, and boron for substrates comprising various transition metals, metalloids, and simple metals. The multilayered coating includes a diffusion barrier layer which is integral to one surface of the substrate, an oxidation resistant layer disposed above the diffusion barrier layer, and an oxidation barrier layer disposed above the oxidation resistant layer. The coatings may optionally also include a thermal barrier layer disposed on the oxidation barrier layer. The diffusion barrier layer comprises mainly borosilicides. Typically, the borosilicides will contain primarily Mo5SiB2 (T2 phase), although other phases may be present. Typically, the oxidation barrier layer comprises primarily borosilicates of SiO2 and B2O3, although other phases may be present. Typically, the oxidation resistant layer comprises mainly molybdenum silicides, primarily of Mo5Si2 (C11 phase), Mo5Si3 (B) (T1 phase) or combinations thereof. The multilayered structures are formed in situ on the substrates such that they are integrated into the substrates. The
diffusion barrier layer and the oxidation barrier layer are grown by annealing an oxidation resistant coating which is itself integrated into the substrate. Therefore, depending on the annealing conditions, some embodiments of the invention, the oxidation resistant layer is desirably converted completely into two layers; an oxidation resistant layer and a diffusion barrier layer, and is thus eliminated. In such embodiments, the diffusion barrier layer, the oxidation resistant layer and the oxidation barrier layer are disposed against each other and integrated across their interfacial regions.

Each layer in the multilayered coating plays a role in protecting and maintaining the strength of the underlying substrate. The diffusion barrier layer helps to prevent the diffusion of reactive atoms, such as silicon from the oxidation resistant layer, into the substrate where they react with and eventually dissolve the substrate and deplete the oxidation resistant layer. The oxidation resistant layer comprises a material that is capable of forming an oxidation resistant surface oxide layer upon exposure to oxygen. The oxide layer grown from the oxidation resistant layer provides the oxidation barrier layer in the multilayered coating. Thus, the oxidation resistant layer facilitates the formation of an oxidation barrier layer in situ. The oxidation barrier comprises a stable oxide capable of resisting oxidation at high temperatures. The optional thermal barrier layer thermally insulates the underlying coating layers and the substrate material.

The invention further provides a method for the in situ production of a multilayered, oxidation resistant coating on a Mo—Si—B alloy substrate or a substrate having a Mo—Si—B alloy surface character. The method includes the step of exposing the substrate to silicon vapor at a temperature and for a time sufficient to allow the silicon to diffuse into the surface of the substrate to form a molybdenum disilicide layer. The substrate and the molybdenum disilicide layer (the oxidation resistant layer) are then annealed in the presence of oxygen at a temperature and for a time sufficient to produce an oxidation barrier layer on the surface of the molybdenum disilicide layer. During the annealing process, the molybdenum disilicide layer undergoes several conversions. First, the molybdenum disilicide layer is at least partially converted into other molybdenum silicide phases, such as $T_2$. For the purposes of this disclosure these new molybdenum silicide phases along with any remaining molybdenum disilicides are still considered to be part of the “oxidation resistant layer” of the coating. Second, a portion of the molybdenum disilicides are converted into borosilicates which make up a diffusion barrier layer. Finally, the portion of the molybdenum disilicides at the surface of the coating oxidize to form borosilicates which make up an oxidation barrier layer. By adjusting the annealing temperatures and times, the silicon to boron ratio in each of the layers can be carefully controlled. This process results in a multilayered structure where each layer is distinct from, but integrated with its neighboring layers. A thermal barrier layer may be applied to the outer surface of the oxidation barrier layer using convention means, such as thermal spray and spray deposition techniques.

A second aspect of the invention provides substrates coated with an oxidation resistant coating having a smooth compositional gradient which is integrated into the substrate. These coatings have a inner region comprising primarily borosilicates that serves as a diffusion barrier region, an intermediate region comprising primarily molybdenum silicides that serve as an oxidation resistant region and an outer layer comprising of borosilicates that serves as an oxidation barrier region. These regions are analogous to the diffusion barrier layer, the oxidation resistant layer and the oxidation barrier layer of the multilayered structures, however, because these coatings form a continuous compositional gradient, the diffusion barrier region and the oxidation resistant region blend smoothly into each other. Like the multilayered coatings, the gradient coating is integrated into the substrate. Also like the multilayered coatings, the gradient coatings may have a thermal barrier layer disposed on their outer surface.

Another aspect of the invention provides an oxidation resistant borosilicate coating having a reduced boron concentration for a Mo—Si—B alloy substrate or a substrate having a Mo—Si—B alloy surface character. The borosilicate coating is produced by applying a thin film of silicon dioxide to the substrate and annealing the thin film coated substrate at a temperature and for a time sufficient to convert the $SiO_2$ film into a borosilicate coating layer. The $SiO_2$ is desirably amorphous $SiO_2$, however crystalline $SiO_2$ may also be used. The boron concentration in the borosilicate layer so produced is lower than the boron concentration in a borosilicate layer that is formed by the high temperature oxidation of the substrate in the absence of the $SiO_2$ coating. As a result, oxygen transport through the borosilicate coatings of this invention is substantially reduced in comparison to the oxygen transport of naturally occurring borosilicate coatings formed through high temperature oxidation of the substrate. In addition, in certain embodiments, the borosilicate layer having a reduced boron concentration may be produced without the formation of an intermediate $MoO_2$ layer between the borosilicate and the substrate which supports the formation of the coating as a barrier to oxygen transport through the surface layer.

Further objects, features and advantages of the invention will be apparent from the following detailed description when taken in conjunction with the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In the drawings:

FIG. 1 shows a schematic illustration of a multilayered, oxidation resistant coating on a Mo—Si—B alloy substrate in accordance with the present invention.

FIG. 2 (a) shows a BSE image of an as-Si packed Mo-14.2Si-9.6B (at %) alloy, (b) shows the XRD scanning results of the as-Si packed sample showing $MoSi_2$ phase, and (c) shows the XRD of the same sample at low intensity indicating the MoB phase.

FIG. 3 (a) shows an SE image of the as-pack cemented samples showing (1) the sub-micron dispersoids and (2) the eutectoid-like growth front, (b) shows a TEM image of the boride particle in the $MoSi_2$ phase matrix, (c) shows a higher-resolution TEM image of the particle showing the high density of stacking faults associated likely with the $alpha$ phase transition.

FIG. 4 shows the oxide thickness variation upon annealing time at 1200° C, with and without coating.

FIG. 5 shows a BSE image of a silicide coated Mo—Si—B alloy exposed at 1300° C, for 25 hr in air (a) shows the developed borosilicate outer layer (Bar in the inlet marks 3 µm), (b) shows the phase transformation of Mo, (c) shows a schematic figure of the marked area in (b), and (d) shows a schematic Mo—Si—B phase diagram (Mo rich corner) indicating the development of phase evolution upon oxidation testing.

FIG. 6 shows a cross section of titania-coated Mo—Si—B substrate subjected to oxidation at 1200° C for 100 hours. The titania was deposited using thermal spray processing.

FIG. 7 (a) shows a back-scattered image of Si-pack cementation coating in the three-phase substrate of $BCC+T_2+T_1$ phases in Mo—W—Si—B alloys. The transformation of the three phases into (Mo, W)$Si_2$ also allows for the formation of
a reactive diffusion zone as depicted in with the main feature of not-completely transformed BCC (bright phase) and Ti phases dispersed in the phase mixture with (Mo, W)Si3 as the matrix.

FIG. 8 shows a SEM back scattered image of (a) as-cast Mo-14.2Si-9.6B (at %) alloy, (b) cross section of Mo-14.2Si-9.6B (at %) alloy oxidized at 1000°C for 100 hr in air, and (c) component X-ray maps of (b).

FIG. 9 shows XRD results showing the presence of mostly amorphous borosilicate, MoO3, and Mo.

FIG. 10 shows (a) TEM image and diffraction pattern for the MoO3 precipitate formed in the in-situ borosilicate layer (outer layer), (b) HR-TEM image of the rectangle area in (a).

FIG. 11 shows (a) a cross section BSE image of the Mo-14.2Si-9.6B (at %) alloy oxidized at 1200°C. For 100 hr in air, (b) a schematic illustration of the diffusion pathway indicating the phase evolution upon oxidation of a Mo—Si—B alloy located in the Mo—Mo5Si3—T1 three phase field (virtual diffusion path between borosilicate and MoO3 is also indicated). (The numbers indicate: (1) Mo(ss) phase with internal oxide precipitates, (2) MoO3, and (3) borosilicate layer. The region below (1) in (a) is the alloy substrate.)

FIG. 12 is a cross-section BSE image of (a) crystal SiO2 powder and (b) amorphous SiO2 powder sprayed Mo-14.2Si-9.6B (at %) alloy following oxidation at 1200°C for 100 hr. (The numbers in each figure indicate: (1) Mo(ss) phase with internal oxide precipitates, (2) MoO3, and (3) borosilicate layer. The region below (1) is the alloy substrate.)

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides coatings for various transition metal-containing substrates, and methods for producing the coatings. The coatings may be multilayered, multiphase coatings comprising oxidation resistant layers and diffusion barrier layers wherein the various layers are substantially distinct from each other. Alternatively, the coatings may be contiguous, multiphase coatings having a compositional gradient and including regions that act as oxidation resistant regions and regions that act as diffusion barriers. The coatings are integrated into the substrates.

A broad variety of substrates may benefit from the coatings of the present invention. The coatings may be grown on any substrate having phase types of molybdenum (BCC), molybdenum silicides (A15 or T1 or C11 or combinations thereof), and molybdenum borosilicides (T1 or T1 or Cl 1 or combinations thereof). This criterion is met for many substrates that have a Mo—Si—B alloy character. (For the purposes of this disclosure, a surface has a Mo—Si—B alloy character if the surface includes enough Mo, Si, and B to permit the in situ growth of molybdenum silicide phases in the surface region of the substrate upon exposure to Si atoms at elevated temperatures. In either case, the surface of the substrate is desirable rich in molybdenum. Substrates suitable for surface enrichment are those in which a solid solution chemical mixture may be formed between at least one of the coating elements (Mo, Si, B) and at least one of the elements in a substrate in at least one of the phases of the coating system (e.g. α-Mo (BCC), T1, Mo5Si3, T1, or MoSi2). This criterion is met for many substrates composed of transition metals, metalloids, simple metals, or combinations thereof. The substrate may be an alloy or a substantially pure metal. The ability of transition metals, metalloids, and simple metals to form solid solutions with these coating elements is discussed in "Handbook of Ternary Alloy Phase Diagrams", ed. P. Villars; A. Prince; and H. Okamoto, (Materials Park, Ohio: ASM International, 1995), which is incorporated herein by reference.

Suitable transition metals for use as or in the substrates include V, Nb, Ta, Ti, Zr, Hf, Fe, Mn, Co, and the like. Suitable metalloid or simple metals include Al, Ga, In, C, Ge, Sn, P and the like. Refractory metals and refractory metal alloys are a group of transition metals that are desirably used as substrate materials.

The enrichment of the substrate surface may be accomplished by exposing the substrate to Mo, Si, and/or B under conditions that promote the mixing of the Mo, Si, and/or B with the underlying substrate. Enrichment of the chemical composition of the surface regions of the substrate can take place using individual elements of Mo, Si or B or combined elements of Mo—Si, Mo—B, Si—B or Mo—Si—B. Methods for enriching a substrate with Mo, Si, and B are well known and include, but are not limited to, pack cementation and chemical vapor deposition. The deposited elements may be mixed with the substrate using conventional solid state annealing techniques. Typically, the solid state annealing will take place at temperature of at least 900°C for at least 24 hours. Higher temperatures and longer times favor faster reaction kinetics. The choice of enrichment elements or compositions will depend on the nature of the underlying substrate. For example, a substrate of a titanium-silicon-aluminum alloy would require enrichment with molybdenum and boron. A substantially pure titanium substrate, on the other hand, would require enrichment with molybdenum, silicon, and boron.


Mo—Si—B alloys provide non-limited examples of substrates that benefit from the coatings of the present invention. Such alloys are well-known in the art. These alloys include both two and three phase alloys, however due their superior oxidation resistance, three phase alloys will likely be the focus for many applications of the coatings provided by this invention. For example, the Mo—Si—B alloy may include α-Mo, Mo5Si3, and Mo5Si2 phases. Alternatively, the alloy may include Mo5Si3, Mo5Si2, and Mo5Si phases. Yet another suitable alloy substrate is made from Mo5Si3, Mo5Si2, and Mo3B phases. More detailed descriptions of molybdenum silicide based substrates for use in the coating systems of the present invention may be found in U.S. Pat. No. 5,595,616;
the silicon atoms migrate into the substrate. To facilitate the means, such as by pack cementation or chemical vapor deposition, a volatile compound that evaporates from the structure leaving vapor under conditions which allow the Si to diffuse into at least one surface rich in silicon and boron (which diffuses up from the substrate to be used in high temperature applications. As shown in FIG. 1, the coating 20 is constructed from a diffusion barrier layer 22 disposed on and integrated into the alloy substrate 24, an oxidation resistant layer 26 above the diffusion barrier layer 22, an oxidation barrier layer 28 on the oxidation resistant layer 26, and optionally a thermal barrier layer 30. The substrate, the diffusion barrier layer, the oxidation resistant layer and the oxidation barrier layer, form a multilayered structure where each layer is integrated with its neighboring layers. This construction is advantageous because it prevents cracking, peeling, and delaminating under extreme operating temperatures and pressures.

The oxidation barrier layer 28, the oxidation resistant layer 26, and the diffusion barrier layer 22 are grown from the substrate 22 in situ. This is advantageous because in situ growth eliminates abrupt interfaces between the layers in the coating which tend to separate at elevated temperatures, weakening the structure.

A oxidation resistant layer 26 comprising molybdenum disilicide (MoSi2) may be grown on a substrate surface having a Mo—Si—B character 24 by exposing the substrate to Si vapor under conditions which allow the Si to diffuse into at least one surface of the substrate where it reacts with Mo to form MoSi2. This may be achieved by conventional means, such as by pack cementation or chemical vapor deposition. In pack cementation the MoSi2 layer is formed by depositing silicon onto the surface of the substrate and heating the components in a furnace. During the heat treatment, the silicon atoms migrate into the substrate. To facilitate the reaction between the Mo and the Si, the substrate will typically be heated to a temperature of at least about 800° C. and the reaction should be allowed to proceed for at least about 24 hours. This includes deposition methods where the substrate is heated to about 900° C. for at least 48 hours. For thicker coatings, annealing can be done at either higher temperatures, longer times, or both.

An oxidation barrier layer 28 is produced in a second annealing step wherein the MoSi2 is annealed in the presence of oxygen at high temperatures to form borosilicates at the surface of the MoSi2 layer. At the same time, at least a portion of the MoSi2 layer is converted into other molybdenum silicates, such as T1 phases, which are incorporated into the oxidation resistant layer along with the remaining MoSi2. Simultaneously, at the elevated annealing temperature a portion of the MoSi2 above the alloy substrate is converted to the T2 phase. This T2 phase layer between the alloy substrate 24 and the oxidation resistant layer serves as the diffusion barrier layer 22.

The oxidation barrier layer forms as follows: during the annealing process a portion of the MoSi2 produces MoO3, a volatile compound that evaporates from the structure leaving a surface rich in silicon and boron (which diffuses up from the underlying substrate) which react to form a protective borosilicate scale. The resulting borosilicate scale is predominately made from SiO2 with a smaller concentration of B2O3. The presence of B2O3 in the scale is advantageous because it decreases the viscosity of the borosilicate layer, providing enough flow to heal small cracks or defects that appear in the layer. This is desirable because it allows the structure to self-heal from damage caused by the impact of foreign objects. However, too much boron in the borosilicate layer will reduce the oxidation resistance of the barrier. Therefore, the coatings should have a boron:silicon ratio that is low enough to provide a barrier to oxidation. In some embodiments the boron concentration in the oxidation barrier layer 28 is no more than about 25 atomic percent. This includes embodiments wherein the boron concentration in the oxidation barrier layer 28 is no more than about 10 atomic percent, further includes embodiments wherein the boron concentration in the oxidation barrier layer 28 is no more than about 6 atomic percent, and still further includes embodiments wherein the boron concentration in the oxidation barrier layer 28 is no more than about 3 atomic percent.

The diffusion barrier layer 22 is produced during the annealing process serves to prevent or hinder the diffusion of silicon atoms from the oxidation barrier layer 28 and the oxidation resistant layer 26, which have relatively high Si concentrations, to the underlying substrate 24 which has a lower Si concentration. This is desirable because the continued exposure of the alloy substrate to Si atoms would eventually lead to the dissolution of the substrate and depletion of the oxidation resistant layer 26. The T2 phase layer provides a low mobility of silicon transport that prevents or hinders the diffusion of silicon from the upper coating layers to the underlying alloy substrate 24. The thickness of the diffusion barrier layer 22 may have a range of values.

The annealing temperature for the formation of the oxidation barrier layer 28 and diffusion barrier layer 22 may be higher than the temperature at which the oxidation resistant layer 26 is initially formed. In various embodiments the annealing temperature may be at least 800° C. or even at least 1000° C. The annealing time may be at least 24 hours. In some embodiments, the total thickness of the diffusion barrier layer, the oxidation barrier layer and any oxidation resistant layer will be at least 20 microns, but in other embodiments the total thickness may be greater.

The multilayered, oxidation resistant coatings of the present invention may optionally include an overlying thermal barrier layer 30 which thermally insulates the underlying coating layers and the alloy substrate 24 by producing a temperature drop across the thermal barrier layer. As a result, the operating temperature capabilities of the material so insulated are extended. The thermal barrier layer 30 typically comprises a heat resistant ceramic and is generally characterized by a low thermal conductivity and, preferably, low oxygen diffusivity. In addition, the material comprising the thermal barrier layer 30 and the oxide comprising the underlying oxidation barrier layer 28 should have similar coefficients of thermal expansion. This reduces the thermal stress at the interface at elevated temperatures and prevents cracking of the thermal barrier layer 30 or separation of the thermal barrier layer 30 from the oxidation barrier layer 28.

Ceramics suitable for use as thermal barriers include, but are not limited to, zirconia, stabilized zirconia, Al2O3, mullite, C60-Sr0.5Zr0.5P2O7, Ca0.5Sr0.5Zr4P6O24, and combinations thereof. In addition, the inventors have discovered that TiO2 is particularly well suited for use with multilayered coatings grown on molybdenum silicide based alloys because TiO2 has a coefficient of thermal expansion close to that of the SiO2 in the borosilicate oxidation barrier layer and is able to exist in equilibrium with the SiO2.

The thermal barrier layer 30 may be deposited by conventional techniques, including thermal spray techniques, such as plasma spray, and vapor deposition techniques, such as electron beam physical vapor deposition. The desired thick-
ness of the thermal barrier layer will depend on the intended application for the metal alloy substrate.

A second aspect of the invention provides substrates coated with an oxidation resistant coating having a smooth compositional gradient which is integrated into the substrate. The first step in producing these gradient coatings is to alloy a Mo—Si—B alloy substrate or a substrate having a Mo—Si—B alloy surface character with a phase modifier element. If the substrate is a Mo—Si—B alloy, suitable substrates may be formed by alloying a the phase modifier element with the molybdenum, silicon, and boron during the production of the substrate. Alternatively, the phase modifier may be alloyed with the substrate during the process of enriching the surface of the substrate with molybdenum, silicon, and/or boron. For example, when the substrate does not initially contain molybdenum, silicon, and/or boron, the surface of the substrate can be enriched with one or more of these elements using solid state annealing techniques, such as pack cementation, to produce a substrate having a Mo—Si—B alloy surface character, as described above. The phase modifier element may be added along with the surface enriching elements during this process to produce the alloyed substrate. The resulting alloyed substrate is then contacted with silicon under conditions sufficient to induce the diffusion of silicon into the substrate and the reaction of the silicon with molybdenum in the substrate. Silicon pack cementation is one process that may be used for this purpose. Because the silicon has a different mobility in the various phases of the substrate it reacts with the different phases at different rates to produce a compositional gradient extending from the substrate outward.

The gradient coating comprises primarily borosilicides, such as $T_2$, alloyed with the phase modifier in the region near the underlying substrate and primarily MoSi$_2$ alloyed with the phase modifier in the region near the exterior surface. When exposed to oxygen at elevated temperatures, the alloyed MoSi$_2$ phase oxidizes to form an oxidation barrier layer of borosilicates. The concentration of oxidation resistant phases (or a character of an oxidation resistant layer) in the outer region of the gradient coating is higher than the concentration of the oxidation resistant phases in the inner region of the gradient. Similarly, the concentration of silicon diffusion resistant phases (or a character of a silicon diffusion resistant layer) in the inner region is higher than the concentration of silicon diffusion resistant phased in the outer region. Therefore, the gradient coatings provide resistance toward both oxidation and silicon diffusion.

The phase modifier element may be any transition metal, metalloid, or simple metal that accentuates the difference in mobility of silicon between the various molybdenum, molybdenum borosilicide, molybdenum borosilicide, and molybdenum silicide phases of the substrate. Tungsten is one non-limiting example of a transition metal phase modifier. Other suitable phase modifiers include, but are not limited to hafnium, niobium, and titanium.

Another aspect of the invention provides a protective borosilicate coating having a reduced boron concentration for a transition metal substrate or a transition metal alloy substrate having an Mo—Si—B alloy surface character. One example of a suitable transition metal alloy substrate is a Mo—Si—B alloy substrate. These protective coatings use a thin SiO$_2$ film to improve upon the oxidation resistant coatings that naturally form on the surface of substrates having a Mo—Si—B alloy surface character upon oxidation at high temperatures by reducing the boron concentration in the resulting borosilicates.

Mo—Si—B alloys will naturally form an oxidation resistant borosilicate layer when allowed to oxidize at high temperatures. This process has been described for the three phase Mo, Mo$_2$Si, Mo$_3$Si system by Park et al. in Scripta Materialia, 46, 765-770 (2002), which is incorporated herein by reference. Briefly, oxidation of the Mo—Si—B alloys initially leads to MoO$_3$ formation, but the MoO$_3$ layer offers no protection to continued oxidation. In fact, MoO$_3$ is a highly volatile species that vaporizes from the surface at temperatures above about 750°C, leaving a surface enriched in Si and B that develops a protective SiO$_2$ layer containing some B$_2$O$_3$ (i.e., the borosilicate layer) at high temperatures (i.e., temperatures of about 1000-1200°C). The borosilicate surface layer does restrict oxygen transport and provides a reduced oxygen activity so that a stable MoO$_2$ phase forms at the substrate alloy surface. This borosilicate scale so produced is protective, but it does not completely block oxygen transport so that with continued oxidation exposure, the thickness of the exterior scale increases along with a recession in the alloy substrate.

The present invention provides an improved borosilicate coating which was made possible, at least in part, by the inventors’ discovery that by enriching the SiO$_2$ content of the outer borosilicate layer the oxygen activity and the oxygen transport through the coating can be reduced. This may be accomplished by shifting the equilibrium of the coating from a borosilicate+MoO$_3$ system, as described above, towards a SiO$_2$+Mo system.

A borosilicate that is enriched in SiO$_2$ (i.e., having a reduced boron concentration) may be produced in accordance with the present invention by applying a thin film of SiO$_2$ to at least one surface of a Mo—Si—B alloy substrate and annealing the SiO$_2$ coated substrate at a temperature and for a time sufficient to form a borosilicate scale on the substrate. In some embodiments the formation of the borosilicate scale is accompanied by the formation of a Mo phase having internal oxide precipitates between the substrate and the borosilicate. The resulting scale will have a boron concentration that is lower than the boron concentration of a borosilicate scale formed through the high temperature oxidation of the substrate in the absence of the SiO$_2$ thin film. In some embodiments the boron concentration in the borosilicate coating is less than 5 atomic percent. This includes embodiments where the borosilicate coating contains less than about 5 atomic percent, further includes embodiments where the borosilicate coating contains less than about 4 atomic percent, and still further includes embodiments where the borosilicate coating contains less that about 3 atomic percent. In some embodiments, the borosilicate coating is formed without the formation of a MoO$_3$ layer between the substrate and the borosilicate coating.

The SiO$_2$ may be applied to the surface of the alloy substrate by conventional deposition techniques. These techniques include, but are not limited to powder spraying, thermal spray deposition, and chemical vapor deposition. The applied SiO$_2$ film may be quite thin. Once the film is applied, or during the application of the film, the substrate and the SiO$_2$ are annealed at a temperature and for a time sufficient to produce the borosilicate coating. The annealing temperature and time will vary depending on a variety of factors, including the SiO$_2$ film thickness, the method of SiO$_2$ deposition and substrate used. Exemplary annealing temperatures and times include, but are not limited to, annealing temperature of at least 800°C for annealing times of at least 24 hours.

The Mo—Si—B alloy substrates that may benefit from the borosilicate coatings having reduced boron concentrations
include the two and three phase Mo—Si—B alloys listed above with respect to the multilayered, oxidation resistant coatings.

EXAMPLES

Example 1

Formation of a Multilayered, Oxidation Resistant Coating on a Three Phase Mo—Si—B Alloy Substrate

Si pack cementation process was employed to produce a MoSi$_2$ oxidation resistant layer. A powder mixture of 70 wt% Al$_2$O$_3$, 25 wt% Si, and 5 wt% NaF were loaded in an alumina crucible together with clean alloy pieces (Mo-14.2Si-9.6B) followed by sealing with an Al$_2$O$_3$ slurry bond. The sample crucible was annealed at 900° C. for 48 hours in an Ar atmosphere. The detailed procedure is described in S. R. Levine and R. A. Caves, J. Electrochem. Soc.; Solid-State Science and Technology. 121, 1051 (1974) and A. Mueller, G. Wang, R. A. Rapp, E. L. Courtright and T. A. Kircher, Mat. Sci. Eng., A155, 199 (1992). Briefly, the process involves the deposition of Si vapor carried by volatile halide species on the substrate embedded in a mixed powder pack at the elevated temperature, which consists of a halide salt activator and an inert filler.

A BSE image of an as-Si packed sample is shown in FIG. 2(a). The nominal thickness of the MoSi$_2$ layer was observed as about 10 µm. During the Si pack cementation process, the inward Si diffusion to the substrate results in the formation of mainly the MoSi$_2$ phase. The reactively formed MoSi$_2$ layer was also confirmed by XRD (FIG. 2(b)). The reactive MoSi$_2$ layer formation in a diffusion couple between pure Mo and Si has been reported previously (see, for example, P. C. Totorici and M. A. Dayananda, Scriv. Mater. 18, 3863 (1998); and P. C. Totorici and M. A. Dayananda, Metall. Mater. Trans. A. 38, 545 (1999)), where the intermediate silicides follow parabolic growth upon diffusion annealing and the growth of the Mo$_3$Si phase is sluggish. Also, silicon, instead of molybdenum, mainly contributes to the formation of the MoSi$_2$ phase and other silicides, which is consistent with the pack cementation observation (i.e. inward diffusion of Si).

Silicon is the main diffusing element into the substrate during the pack cementation process, resulting in the formation of the MoSi$_2$ outer layer. However, the MoSi$_3$ phase is in equilibrium with the MoB and T$_1$ phases in the ternary Mo—Si—B system (see FIG. 2), which is different than the phase combination of the as-cast alloy composed of Mo, MoSi$_2$ and T$_2$. This suggests that other phases exist between the MoSi$_2$ coating and the substrate when a local equilibrium holds during the interface reactions. Furthermore, the relatively slow mobility of Mo and B at this temperature particularly in the T$_2$ phase appears to suggest that a boride phase must accompany the formation of the MoSi$_2$ layer structure. A further examination of the cross section of the as-packed sample in a high-resolution Field Ion SEM following etching with a Murakami solution reveals the presence of sub-micron size particles (marked as 1 in FIG. 3(a)) that are highly etched and dispersed quite uniformly within the MoSi$_2$ layer. Furthermore, there is a reaction front beneath the outer MoSi$_2$ layer that appears to exhibit euctectoid-like structures. EDS (Energy-Dispersive Spectroscopy) examination on the dispersed showed an absence of silicon. However, since boron can not be detected in EDS and the particle is too small, a structural examination via TEM was used in order to verify the types of borides formed. The TEM examination was conducted on samples that were annealed at 1200°C for 24 hours following the coating treatment. The TEM evaluation clearly reveals the presence of MoB particles within the MoSi$_2$ (FIG. 3(b)). The large presence of twin boundaries is clearly evident in the high resolution TEM image (FIG. 3(c)). The large density of twins may be developed from the polymorphic phase transition between alpha and beta MoB. Thus, it appears that the reactive Si diffusion into the substrate may stabilize the beta-MoB phase initially, which then transformed into the alpha MoB phase through a polymorphic phase transition. The growth front beneath the MoSi$_2$+MoB particle layer appears to involve at least the MoB phase (marked 2 in FIG. 3(a)). In addition, the Mo$_3$Si$_2$(B) or T$_1$ phase is more likely to be the second phase present in the growth front since the T$_1$ phase is the only phase that is in equilibrium with the MoSi$_2$, MoB and two phases from the substrate (Mo$_3$Si and T$_2$ phase). The silicon reactive diffusion can immediately blanket the Mo(ss) phase and transform it into the Mo$_3$Si phase resulting the growth front to proceed quite uniformly into the substrate.

Upon oxidation of MoSi$_2$ coatings on transition metals at high temperature, the MoSi$_2$ coating layer is transformed into Mo$_3$Si$_2$(on the substrate side) and SiO$_2$ (on the free surface of MoSi$_2$ coating layer) as well, indicating that silicon depletion is a significant factor for determining the molybdenum disilicide coating lifetime. Also, it should be noted that the growth of the SiO$_2$ layer is about 2-3 orders of magnitude slower than that of the Mo$_3$Si$_2$ interlayer, suggesting that silicon depletion mainly contributes to impeding the growth of the Mo$_3$Si$_2$ phase. In order to retard the growth of the Mo$_3$Si$_2$(T$_1$) phase consuming the molybdenum disilicide coatings, the effect of other elements such as Ta or Ge has been documented. For example, the rate constant of Mo$_5$Si$_3$ phase is about 2 times faster than (Mo, Ta)$_3$Si$_3$ phase at 1400° C. and the rate constant differences expand with increasing annealing temperature.

While the retardation of Mo$_3$Si$_2$(T$_1$) growth can be achieved by selected alloying additions, the main limitation still resides in the fact that the T$_1$ phase exhibits a poor oxidation resistance. Recently, it has been reported that B addition to T$_1$ phase increases the oxidation resistance significantly. The Boron-doped Mo$_3$Si$_2$(T$_1$) thin layer exhibits a superb high temperature oxidation resistance (see R. W. Bartlett and P. R. Gage, Trans. of Metall. Soc. of AIME, 230, 1528 (1964)). The implication of these results appears to be that the MoSi$_2$ layer coating is suitable for the Mo—Si—B alloys. Although the growth of the T$_1$ phase may still be high upon high temperature exposure, it can be as an excellent protective coating provided that the T$_1$ phase is saturated with B during the high temperature oxidation exposure.

Upon oxidation test of the silicide coated samples, a thin oxide layer formed at the outer layer. On this layer several elements of Al, Na, Si and O were identified by EDS, in which Na is a byproduct from NaF during pack cementation. While Al$_2$O$_3$ may also be present (from residual pack cementation powder), the oxide scale formed was mainly composed of SiO$_2$. The observed typical thickness of the scale after the oxidation test at 1200°C for 100 hours was less than 5 µm. Upon oxidation at 1200°C, the synthesized MoSi$_2$ phase had completely transformed into Mo$_3$Si$_2$(T$_1$) when the exposure time reached 50 hr. While the Mo$_3$Si$_2$ phase did start to form within the T$_1$ phase on this sample upon further annealing, the depletion of Si on the surface which results in the Mo$_3$Si$_2$ phase formation was quite slow, since the oxide layer is very thin. This implies that the T$_1$ phase coating indeed serves as an effective protective layer due to the boron content. With further oxidation exposure up to 100 hours at 1200°C, the T$_1$ phase coating appears to remain stable and retain an excellent
the excellent oxidation resistance of the T\textsubscript{1} phase coating even
thermore remains intact with the substrate. In contrast, the
non-coated sample, while the thickness is about 5 µm for
the coated sample, which clearly shows an excellent oxidation
resistance compared to the non-coated sample.

The transformation of MoSi\textsubscript{2} into Mo\textsubscript{5}Si\textsubscript{3} phase has been
reported previously for the diffusion annealing of Mo
with a MoSi\textsubscript{2} coating (see T. A. Kir and E. L. Courtright El.,
Mat. Sci. Eng., A155, 67 (1992)). The annealing treatment
was not conducted in air in this case, since without B
addition to the MoSi\textsubscript{2} phase the coating has a poor oxidation
resistance. The extrapolated value of the MoSi\textsubscript{2} parabolic
growth parameter, k (x=kYt), in the MoSi\textsubscript{2}, coated Mo sample is about
4.0x10\textsuperscript{-6} (cm/Vsec) at 1200°C. which is significantly larger
than the estimated k value of about 9x10\textsuperscript{-6} (cm/Vsec) in
the current work at 1200°C. In fact, the growth kinetics of the
MoSi\textsubscript{2} phase is closely related to the Si transport towards
substrate, instead of towards the free surface. It is considered
that the slow kinetics in the current work is related to the layer
developed between T\textsubscript{2} and substrate with the associated boron
content.

It is also worth noticing that the thickness of the MoSi\textsubscript{2} phase
for these experiments does not show a considerable thickness change
even after a complete elimination of the MoSi\textsubscript{2} phase. This suggests that while the rapid growth of the
T\textsubscript{2} phase in replacing the MoSi\textsubscript{2} phase is similar to the case of
binary Mo—Si system, the change in the T\textsubscript{2} phase layer
thickness is essentially stalled afterwards. This implies that
there must be an effective diffusion barrier formed underneath
the T\textsubscript{2} phase coating inhibiting Si diffusion inward into the
substrate and hence consuming the T\textsubscript{2} phase coating.

The synthesized MoSi\textsubscript{2} phase is not in equilibrium with the
three-phase area. The capability of (boro)silica with a potential thermal barrier oxide
such as titania. The coating system can be further modified for example with pack cementation treatment which produces
silicide phases that naturally form silica when exposed to high temperatures.

Example 2

Preparation of an Oxidation Resistant Gradient
Coating on a Mo—Si—B Alloy

It has been shown recently that a small amount of a transition metal phase modifier, such as tungsten, alloyed with the
coatings made from molybdenum, silicon, and boron, can alter the phase equilibrium of a Mo—Si—B system so that a
three-phase field of BCC+T\textsubscript{2}+T\textsubscript{1} can be stabilized (see R.
Sakidja, S. Kim, J. S. Park and J. H. Perepezko, in Defect Properties and Related Phenomena in Intermetallic Alloys,
E. P. George, H. Inui, M. J. Mills and G. Eggeler, Editors, p. BB2.3.1, MRS, Warrendale, Pa. (2003)). By coupling the
alloying addition with the Si-pack cementation, a new coating structure has been synthesized as exemplified in FIG. 7. The
coating consists of the (Mo, W)Si\textsubscript{2} phase as the outermost layer with a multiple phase reaction composed of mostly of
the (Mo, W)Si\textsubscript{2} phase (dark phase). The capability of W
substitution to accentuate the different mobility of silicon in the
three phases is clearly demonstrated in this case. Unlike the
T\textsubscript{1} phase which has transformed into the disilicide phase,
the T\textsubscript{2} and BCC phases have not fully transformed. In this
case, the diffusion front is described by the different reaction
paths that are followed by each phase:
The method of claim 1, wherein the substrate is a Mo—Si—B alloy.

3. The method of claim 2, wherein the coating has a layered structure comprising an external layer of borosilicate scale and an internal layer comprising a molybdenum phase with internal silicon oxide precipitates, the internal layer disposed between the substrate and the external layer.

4. The method of claim 1, wherein the substrate has a Mo—Si—B surface character.

5. The method of claim 1, wherein the concentration of boron in the borosilicate scale is lower than the boron concentration of a borosilicate scale formed through high temperature oxidation of the substrate in the absence of the silicon dioxide.

6. The method of claim 1, wherein the concentration of boron in the borosilicate scale is less than about 6 atomic percent.

7. The method of claim 1, wherein the concentration of boron in the borosilicate scale is less than about 3 atomic percent.

8. The method of claim 1, wherein the silicon dioxide is a silicon dioxide powder.

9. The method of claim 1, wherein the coating has a layered structure comprising an external layer of borosilicate scale and an internal layer comprising a molybdenum phase.
prising molybdenum with internal silicon oxide precipitates, the internal layer disposed between the substrate and the external layer.

10. The method of claim 1, further comprising forming the substrate comprising molybdenum and boron by exposing a substrate comprising molybdenum to boron under conditions that promote the reactive mixing of the molybdenum and boron.