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(54) Title: ALPHA Al2O3 AND Ti2O3 PROTECTIVE COATINGS ON ALUMINIDE SUBSTRATES

(57) Abstract: A titanium aluminate substrate (4) is vulnerable to air oxidation, limiting the use of this substrate in a variety of industrial applications, including the aircraft and aerospace industries. A bilayer reactive barrier (2) is formed on a titanium aluminate substrate. The barrier layer includes an \( \alpha-Al_2O_3 \) layer (6) from the reaction of oxygen from the disassociation of water with alumina in a gaseous and water vapor atmosphere at high temperatures and low oxygen concentration. During the process, titanium migrates through the \( \alpha-Al_2O_3 \) to a gas/barrier layer surface (14) and is oxidized to form a \( Ti_2O_3 \) layer (8). A surface of the \( Ti_2O_3 \) layer is subsequently oxidized to form a \( TiO_2 \) layer (12). In this manner, a triple layer barrier is formed in which the immersible \( TiO_2 \) and \( \alpha-Al_2O_3 \) are separated by \( Ti_2O_3 \). The three layers are bonded to each with a bond strength greater than 69,000 kPa.
ALPHA AL₂O₃ AND Ti₂O₃ PROTECTIVE COATINGS ON ALUMINIDE SUBSTRATES

Background of the Invention

The present invention relates to processes for forming barrier layers on metal surfaces. It finds particular application in conjunction with forming barrier layers on titanium and aluminum containing substrates, particularly titanium aluminides, which resist oxidation, resist corrosion, resist wear and abrasion, and resist corrosive media.

Titanium aluminide is currently being investigated to replace super alloys for use in aircraft turbine engines and aircraft structures. Titanium aluminide is about half the density of superalloys of comparable strength, so a large reduction in aircraft weight is possible. The titanium aluminide alone is quite brittle, but workers have been able to add other elements to reduce this brittleness. A remaining development problem is that the oxidation resistance of these titanium aluminide compounds is lower than desired at elevated temperature. Therefore, a key factor in increasing the maximum use temperature is the enhancement of oxidation resistance while maintaining creep and strength performance.
Previous attempts to develop a protective coating have resulted in coatings which are unstable or tend to peel off. If a titanium aluminide substrate is oxidized in air or oxygen at high temperature, as is conventionally done, $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$ are formed. These two oxides have different structures and are immiscible in each other. As such, the mixed oxide is porous and weakly bonded to the substrate. Therefore, they are subject to spallation from the substrate. As such, the oxides are not an effective oxygen barrier. That is, they do not prevent the diffusion of oxygen into the substrate and the reaction of oxygen with aluminum, titanium, and other elements below the surface.

The present invention relates to a new and improved technique for forming strongly-bonded surface barriers for titanium aluminide substrates, which overcomes the above-referenced problem, and to the structures produced by such a technique.

**Summary of the Invention**

In accordance with one aspect of the present invention, a specific reactive element barrier is formed on a titanium aluminide substrate. A gaseous atmosphere is created with a concentration of water vapor below 750 ppm at a temperature above about 550 °C contiguous to a surface of the titanium aluminide substrate on which the barrier layer is to be formed. The gaseous hydrogen and water vapor are reacted with aluminum and titanium specific reactive elements at the substrate surface to form an aluminum oxide layer strongly bonded to the substrate surface. The temperature and water vapor concentration are maintained within these ranges. The gaseous hydrogen/water vapor atmosphere is reacted with the specific reactive elements at the substrate surface with oxygen to form a specific reactive element. The barrier layer is strongly bonded to the substrate surface.
and has aluminum oxide at a substrate/barrier layer interface.

In accordance with another aspect of the present invention, a barrier layer protected titanium aluminide material is provided. An aluminum oxide layer is bonded to a surface of a titanium aluminide substrate.

One advantage of the present invention is that it provides a barrier that is resistant to permeation by oxygen.

Another advantage of the present invention is that it forms a barrier which resists wear.
Yet another advantage of the present invention is that it forms a surface barrier which inhibits erosion.
Still another advantage resides in the strong adhesion of a barrier layer to a titanium aluminide substrate.

Still further advantages and benefits of the present invention will become apparent to those of ordinary skill in the art upon reading and understanding the following detailed description of the preferred embodiments.

**Brief Description of the Drawings**
The invention may take form in various components and arrangements of components, and in various steps and arrangements of steps. The drawings are only for purposes of illustrating preferred embodiments and are not to be construed as limiting the invention.

FIGURE 1 is a Ti-Al phase diagram, giving a graphic description of the weight percent (atomic percent) of aluminum vs. temperature (°C) in typical Ti-Al substrates;

FIGURE 2 is a drawing illustrating the multilayer characteristics of the oxide coating;

FIGURE 3 is an ESCA depth profile demonstrating changes in the concentration of titanium as Ti₂O₃ and
aluminum as $\alpha$-Al$_2$O$_3$ with depth from the gas/substrate interface;

FIGURE 4 is an X-ray diffraction study showing only the presence of $\alpha$-Al$_2$O$_3$ and Ti$_2$O$_3$ after processing;

FIGURE 5 is an ESCA depth profile of a Gamma-met titanium aluminide specimen showing reduction of a titanium oxide layer;

FIGURE 6 is an ESCA profile scan showing the presence of $\alpha$Al$_2$O$_3$ as the only oxide present;

FIGURE 7 is an ESCA depth profile showing the absence of a titanium oxide layer; and

FIGURE 8 is an ESCA profile scan showing the presence of titanium metal and absence of titanium oxide.

**Detailed Description of the Preferred Embodiments**

The present application describes the structure and formation of a reactive barrier on the surface of a titanium aluminide substrate. A higher concentration of the specific reactive elements is brought to the surface, and a highly stable oxide of the specific reactive element is formed on the surface of the titanium aluminide substrate. The preferred specific reactive elements present in the immediate invention include aluminum, titanium, and mixtures thereof.

In one embodiment of the present invention, the reactive barrier coating is formed on the surface of the titanium aluminide substrate in a low-oxygen environment. The substrate is heated to an elevated temperature, preferably between about 870 and about 1050 °C, in an environment of hydrogen, with a partial pressure of water vapor, preferably about 1 to about 750 ppm, and more preferably between about 1 to about 500 ppm. The temperature is between about 550 and about 1100 °C. At this temperature and pressure, all non-specific reactive elements on the surface are reduced. As the less stable surface oxides are reduced by hydrogen, aluminum and
titanium atoms are exposed to the fresh oxygen produced by
the dissociation of the water vapor and from the
dissociation of less stable surface metal oxides which
have formed on the substrate. These aluminum and titanium
atoms react with the oxygen to produce strong stable
aluminum and titanium oxides. These specific reactive
element oxides are too stable to be reduced by the
hydrogen/water vapor atmosphere.

The preferred process heats the titanium
aluminide specimens in a hydrogen atmosphere that contains
between about 1 and about 500 ppm of water vapor. Some
substrates may take up hydrogen at lower temperatures.
Therefore, in those cases, after processing the substrates
in the temperature range of about 870 and 1050 °C, and
upon cooling the furnace down to about 815 °C, the
hydrogen atmosphere is evacuated from the furnace and the
cool down process is continued in a vacuum that contains
less than 1 ppm of water vapor. Alternatively, the
furnace is backfilled with an inert gas that contains less
than 1 ppm of water vapor as the furnace is cooled to room
temperature.

In one embodiment of the present invention, the
substrate upon which the reactive barrier is formed is a
titanium aluminide substrate. The phase diagram of
titanium aluminides is shown in Figure 1. As can be seen,
titanium aluminide substrates have attractive elevated-
temperature properties and low density typical of
intermetallic compounds. These attributes make titanium
aluminide materials very interesting for both engine and
airframe applications. These advanced materials are key
to technological advancements, and enhanced structural
materials are particularly vital to advanced aerospace
systems.

Intermetallic compounds, such as titanium
aluminide, are defined as having an ordered alloy phase
between two metallic elements. An alloy phase is ordered
if two or more sublattices are required to describe its atomic structure. The ordered structure of intermetallic compounds exhibits attractive elevated-temperature properties, i.e. strength, stiffness, etc., because of the long-range ordered super-lattice that reduces dislocation mobility and diffusion properties at elevated temperature. The reduced dislocation motion also results in fracture toughness at extremely low ambient temperature.

The immediate process of forming protective oxide coatings on titanium aluminides is effective for all aluminide compounds. This includes the phases $\beta$-Ti, Ti$_3$Al, $\gamma$-TiAl, and TiAl$_3$. Because of their low density, the ordered intermetallic titanium aluminides, especially $\gamma$-titanium aluminide (TiAl) and $\alpha$-2-titanium aluminide (Ti$_3$Al), are particularly attractive candidates for applications in advanced aerospace engine and airframe components, in both monolithic and composite concepts. A comparison of the characteristics of monolithic titanium aluminides with other aluminides and superalloys is shown in Table 1.

Table 1: Melting Points and Densities for Aluminides

<table>
<thead>
<tr>
<th>Aluminide</th>
<th>Melting Point (°C)</th>
<th>Density (gm cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$Al</td>
<td>1600</td>
<td>4.2</td>
</tr>
<tr>
<td>TiAl</td>
<td>1460</td>
<td>3.9</td>
</tr>
<tr>
<td>Fe$_3$Al</td>
<td>1540</td>
<td>6.7</td>
</tr>
<tr>
<td>FeAl</td>
<td>1330</td>
<td>5.6</td>
</tr>
<tr>
<td>Ni$_3$Al</td>
<td>1390</td>
<td>7.5</td>
</tr>
<tr>
<td>NiAl</td>
<td>1640</td>
<td>5.9</td>
</tr>
<tr>
<td>Superalloys</td>
<td>1325-1400</td>
<td>9</td>
</tr>
<tr>
<td>(typical)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In a preferred embodiment, the titanium aluminide substrate is γ-TiAl, that has been modified by the addition of other elements to improve the mechanical properties of the aluminide substrate. The modified γ-TiAl, which has a density of 3.9 g/cm³, less than half the density of typical superalloys is also advantageous. Furthermore, the modified γ-TiAl has a melting point of about 1460 °C, a temperature well above the process temperature required to form the protective oxide coatings of the present invention.

Also preferred are titanium aluminide ternary alloys consisting of Ti-Al-X, where X can be elements such as Cr, Nb, Mn, Mo, W, and V. Some examples of these titanium aluminide ternary alloys are Ti-49Al-2W (atomic %), Ti-44Al-2Mo, and Ti-47Al-29V. Also included in this system are titanium aluminide quaternary alloys consisting of Ti-Al-Nb-Y where Y equals Cr or Mn. In general, the processes for forming oxide barrier layers on titanium and aluminum containing substrates relates to all titanium aluminide ternary and quaternary and higher level alloys that contain elements that have been added to produce certain desirable mechanical improvements to the substrate.

Alternatively, the oxide coatings may be formed on other titanium and aluminum containing substrates. Included is the titanium-aluminum system consisting of the titanium-aluminum alloy disordered alpha phase (α-TiAl) and beta phase (β-TiAl). Superalloys, and other alloys, metals, and materials that contain about 2% or more of aluminum and about 2% or more of titanium are also suitable as substrates upon which to form the protective oxides formed by the present invention.

With reference to Figure 2, a reactive barrier is formed which is a specific reactive element oxide. A titanium aluminide substrate is modified such that the surface of the substrate forms a specific reactive element
oxide film that resists corrosion, permeation by hydrogen isotopes, and serves other useful functions. This oxide protective coating 2 is formed because the intermediate titanium oxide, Ti$_2$O$_3$, not TiO$_2$, is formed with the α-Al$_2$O$_3$. In the low-pressure, high temperature oxygen region provided by the process used, there exists a high solid solubility between both α-Al$_2$O$_3$ and Ti$_2$O$_3$ phases. The two oxide phases have similar lattice constants and the same crystalline structure.

The equilibrium pressure for the formation of α-Al$_2$O$_3$ is below the equilibrium pressure for the formation of Ti$_2$O$_3$ so that an α-Al$_2$O$_3$ layer 6, the more stable oxide, forms directly on the substrate 4 in preference to a Ti$_2$O$_3$ enriched layer 8. In this atmosphere and at process temperature, both aluminum and titanium atoms diffuse from the bulk substrate to the substrate surface, react with the oxygen present there, and form their respective oxides. However, α-Al$_2$O$_3$ is the most stable oxide and bonds strongly to the substrate 4. The titanium oxide on the substrate surface is reduced to titanium by the more reactive aluminum metal present at the surface. As the α-Al$_2$O$_3$ layer 6 grows thicker on the substrate 4 surface, the titanium atoms, reduced from the titanium oxide by the aluminum, diffuse outward toward the oxide/gas interface where they form the oxide, Ti$_2$O$_3$ layer 8. A distinct separation between the α-Al$_2$O$_3$ and TiO$_2$ phases occurs. α-Al$_2$O$_3$ concentrates at an oxide/substrate interface 10 and Ti$_2$O$_3$ concentrates at an oxide/gas interface 12. The Ti$_2$O$_3$ serves to provide a graded interface to reduce the stress caused by any tensile force applied to try and pull the oxide away from the substrate.

When the newly formed oxide coating is then put in air at high temperature and atmospheric pressure as it typically is in an application, a thin coating of TiO$_2$ 14 is formed on the previous gas/oxide interface 12. Since the prior surface coating is mostly Ti$_2$O$_3$, an intermediate
titanium oxide, a thin surface layer of Ti$_2$O$_3$ converts to the layer of fully oxidized TiO$_2$ 14 in air. The amount of TiO$_2$ is insignificant in relation to the amount of Ti$_2$O$_3$ formed. ESCA analysis shows the TiO$_2$ coating is actually very thin, on the order of a few nanometers. The TiO$_2$ coating exists only at the surface of the oxide coating, with a relatively thick graded layer of Ti$_2$O$_3$ existing between the TiO$_2$ layer 14 and the $\alpha$-Al$_2$O$_3$/substrate interface 10.

The separation of $\alpha$-Al$_2$O$_3$ and Ti$_2$O$_3$ phases and formation of the $\alpha$-Al$_2$O$_3$/substrate interface are extremely important discoveries, and can be seen in Figures 3 and 4. Figure 3 is an ESCA depth profile of the immediate oxide coating. As can be seen, the concentration of Ti (as Ti$_2$O$_3$) is greatest at shallower depths, and the concentration of Al (as $\alpha$-Al$_2$O$_3$) is greatest closer to the substrate surface. Figure 4 is an X-ray diffraction study showing the presence of $\alpha$-Al$_2$O$_3$ and Ti$_2$O$_3$ on the substrate surface after processing. This separation shows that the present method forms a strongly-bonded $\alpha$-Al$_2$O$_3$ oxide directly to a titanium-aluminide substrate. The $\alpha$-Al$_2$O$_3$ prevents oxygen from reaching the substrate. Later, when exposed to an air or oxygen atmosphere at a selected higher temperature, the intermediate oxide, Ti$_2$O$_3$, concentrated at the oxide/gas interface, converts to TiO$_2$, but only in small quantities, resulting in a very thin film at the surface. Other elements present in the substrate unable to oxidize in the low-oxygen atmosphere, diffuse into the Ti$_2$O$_3$ region, but remain non-oxidized. The result is a mixed $\alpha$-Al$_2$O$_3$, Ti$_2$O$_3$, and non-oxidized element gradient between the gas/oxide interface 12 and the $\alpha$-Al$_2$O$_3$ oxide barrier 6 on the substrate 4. Such a gradient spreads the load of any applied tensile force over many atom layers making up the thickness of the mixed oxide/non-oxidized element region so that the oxide coating is strongly bonded to the substrate. The $\alpha$-Al$_2$O$_3$,
being the oxide that bonds most strongly to the surface of the substrate, is therefore the actual barrier that prevents oxygen diffusion into the substrate. The relatively thick layer of Ti$_2$O$_3$ between the α-Al$_2$O$_3$ and the TiO$_2$ layers prevents any contact between α-Al$_2$O$_3$ and TiO$_2$, which could cause brittleness, peeling, and spallation.

At least about 2 weight percent of aluminum must be present in the substrate to form the α-Al$_2$O$_3$/substrate oxygen barrier coating with the preferred process. If this limitation is met, the whole range of variation of aluminum with titanium can produce valid protective oxide coatings. The substrates containing the higher percentages of titanium are preferred for their ability to function at higher temperatures.

In another preferred embodiment of the present invention, the oxide coating is a single layer and comprises an α-Al$_2$O$_3$ layer. This layer is formed by following the earlier referenced procedure to establish the α-Al$_2$O$_3$ and Ti$_2$O$_3$ mixed oxide coating. However, instead of stopping the process when the α-Al$_2$O$_3$ is at maximum concentration at the oxide/substrate interface and Ti$_2$O$_3$ is at maximum concentration at the oxide/gas interface, a new process is begun. This new process operates over a temperature range of about 500 °C to 1150 °C with a water vapor concentration range from about 1 to 500 ppm. The water concentration preferably remains low enough to ensure that aluminum can reduce all Ti$_2$O$_3$ present. The Ti$_2$O$_3$ is reduced by the aluminum to titanium and oxygen without interference by other elements present. The oxygen will then react with aluminum to form α-Al$_2$O$_3$ leaving titanium atoms present in the system. There is no titanium concentration gradient to keep the titanium close to the oxide/gas interface, so it will diffuse back to the substrate as titanium atoms seek out vacancies in the substrate region. This leaves a pure α-Al$_2$O$_3$ as the protective oxide.
A preferred system for forming the pure $\alpha$-Al$_2$O$_3$ oxide such as that described above involves a temperature of about 870 °C, over a time period of about 3-6 hours, with a water vapor concentration less than about 50 ppm.

With reference to Figure 5, an ESCA depth profile of a Gamma-met titanium aluminide specimen illustrates what occurs while the Ti$_2$O$_3$ is being reduced to titanium and oxygen by the $\alpha$-Al$_2$O$_3$. Process parameters have been adjusted so that $\alpha$-Al$_2$O$_3$ is the dominant oxide. Aluminum in the region has started the reduction of Ti$_2$O$_3$ in the near-surface region.

In the ESCA process, a sputter-gun continuously sputters away the surface of the specimen at a continuous rate. Also, the specimen is constantly illuminated by X-rays with sufficient energy to overcome the binding energy of photoelectrons from elements or their oxides that are present. While the material is being sputtered away to the depth desired, photoelectrons are emitted and their energy is measured by detectors. A montage of several scans of photoelectron counts/sec as a function of binding energy is taken.

With reference to Figure 6, a scan for aluminum where about 150 scans were taken, beginning at the surface is shown. From the surface to about the oxide/substrate interface it is shown that only $\alpha$-Al$_2$O$_3$ exists because the binding energy of the oxide is indicated. Then, the binding energy of aluminum metal is shown as the scans continue into the substrate.

With reference to Figure 7, an ESCA depth profile of the gamma-met titanium aluminide specimen, taken later in the process, is shown. A high concentration of $\alpha$-Al$_2$O$_3$ is indicated near the surface. The reduction of titanium is also shown in the same area.

With reference to Figure 8, a montage of photoelectron counts/sec vs. binding energy scans for titanium is shown. The titanium shown in the Figure 7
depth profile is in the form of titanium metal in Figure 8. All of the Ti₂O₃ has been reduced to titanium and oxygen. The oxygen has reacted to form α-Al₂O₃. The titanium will subsequently diffuse back into the substrate to fall into the vacancies that exist there, resulting in a pure α-Al₂O₃ oxide coating on the titanium aluminide substrate.

In one aspect of the present invention, the thickness of the oxide coating is important in determining the strength of the coating. X-ray diffraction studies and electron spectroscopy for chemical analysis data have shown that the strength of the oxide coating varies with the thickness of the oxide coating. If the coating is too thin, there is not enough protection against oxidation. If the coating is too thick, it becomes somewhat cumbersome and loses adhesion properties. The optimum thickness of the oxide coating, where both protection from oxidation and strong adhesion properties remain intact, is between about 500 and about 1500 nm. Stud pull test show that the present coating can survive an applied tensile stress greater than about 69,000 kPa. These tests were carried out via the use of a Sebastian V unit to try to pull the oxide from the substrate in a pull test in which a tensile pull rod is bonded to the oxide surface by epoxy.

In another aspect of the present invention, a sulfur scavenger is used prior to the formation of the coating. Free sulfur in a bulk substrate diffuses to the surface and condenses in voids or cavities, reducing the bond strength of any oxide present. One of the benefits of the present technique is the very strong bonds formed between α-Al₂O₃ and the titanium aluminide substrate. These bonds have a strength in excess of 69,000 kPa. Therefore, free sulfur is removed from the surface of the substrate. In the preferred process, a flowing hydrogen gas in a preliminary processing step, at atmospheric
pressure, between about 550 and 1100 °C, and containing about 1 to about 750 ppm water, preferably containing about 1 to about 500 ppm water vapor, reacts with any sulfur that has condensed in voids or cavities at the surface of a substrate. Another hydrogen producing atmosphere is an inert gas such as helium containing preferably less than about 750 ppm of water vapor which produces hydrogen that also reacts with any sulfur in a similar manner. Still another hydrogen producing atmosphere consists only of water vapor, over a partial pressure range of from about 1x10^{-6} to about 1x10^{-2} kPa, which produces hydrogen that also reacts with any sulfur in a similar manner. The interaction of water vapor with aluminum produces oxygen and hydrogen. The oxygen reacts with aluminum to form α-Al₂O₃, and the hydrogen is then available to react with sulfur to form hydrogen sulfide—a gas that is removed with the flowing hydrogen.

In another embodiment of the present invention, a repair method for damaged oxide coatings is provided. Damage to the above-mentioned protective oxide coatings in limited regions can be repaired. For example, removal of a small area of oxide may occur by the impact of a high-velocity particle. Or, two previously processed parts may be welded or brazed together, perhaps by laser welding. The resulting weld lacks a proper protective oxide unless the barrier layer formation process is repeated after the weld was completed. Small region repairs are accomplished by heating the locally damaged surface area in the appropriate environment. Such local heating is preferably accomplished by laser-heating procedures.

A scanning mechanism causes a pulsed laser with variable repetitive pulsing rate to sweep in both the X and Y directions over a selected area. The scanning rates of both the X and Y directions are adjusted to provide uniform heating of the damaged or newly welded area, and also to provide a gradient in temperature.
between the damaged area and the much lower temperature surrounding the oxide protected area. Any laser which operates between ultraviolet and infrared radiation is contemplated. The laser intensity is preferably less than $10^8 \text{ J/sec}^2$ for the ultraviolet wavelengths, and less than $10^{11} \text{ J/sec}^2$ for the infrared light. For laser wavelengths between the UV radiation and infrared radiation, the limiting intensity varies approximately linearly with wavelength. Above the limiting laser intensities given, ablation of material may occur. Only heating is desired, so laser intensities below these limits may perform best.

Importantly, the area to be repaired is encompassed by the above-described environment. Particularly, the environment is hydrogen gas at atmospheric pressure that contains approximately 1 to about 500 ppm of water vapor. Another alternate atmosphere is an inert gas such as helium at atmospheric pressure that contains approximately 1 to about 500 ppm of water vapor. Still another alternate atmosphere consists only of water vapor, over a partial pressure range of from $1 \times 10^{-6}$ to $1 \times 10^{-2}$ kPa.

In another embodiment of the present invention, the process is useful for forming the $\alpha$-$\text{Al}_2\text{O}_3$ protective coating in its unilayer or bilayer form on titanium aluminide substrates when mechanical work and/or heat treatment of the substrate must be accomplished at low temperatures, on the order of about 250 °C or less. Additionally, the repair of damaged coatings often must be carried out at temperatures lower than about 550 °C.

This process is preferably carried out after the initial coating is formed. In one embodiment, a processed part is removed from the furnace and mechanical work and/or heat treatments are performed on the part. After these activities have been completed, the surface must be re-processed to form a final protective $\alpha$-$\text{Al}_2\text{O}_3$ coating on the substrate. This is accomplished by using the pulsed-
laser technique previously described. Specifically, the part is again placed in the processing furnace, preferably equipped with windows that allow a laser beam to be focused upon the substrate, and the furnace is evacuated until the vacuum contains less than about 1 ppm water vapor. The furnace is then back-filled with hydrogen containing less than about 50 ppm water vapor. The substrate is then heated by the furnace to a temperature at which the mechanically-worked and/or heat-treated piece can safely be exposed without damage. The laser beam is then focused upon the part and scanned over the surface that is to be heated to a chosen process temperature between about 550 and 1100 °C. The laser beam may then scan the substrate surface for partial or full coverage as desired. An infrared detector preferably monitors the surface temperature for control of the laser parameters so that the desired surface temperature can be maintained. This process is equally applicable to the formation of the unilayer or bilayer coatings of the present invention. This is true even though the bulk of the substrate will be at the low temperature maintained by the furnace environment.
Having thus described the preferred embodiments, the invention is now claimed to be:

1. A process for forming a specific reactive element barrier (2) on a titanium and aluminum containing substrate (4), preferably a titanium aluminide substrate, the process comprising:

   creating a gaseous atmosphere with a concentration of water vapor below 750 ppm at a temperature above about 550° C contiguous to a surface of the titanium aluminide substrate on which the barrier layer is to be formed (10); and

   reacting the gaseous hydrogen and water vapor with aluminum and titanium specific reactive elements at the substrate surface to form an aluminum oxide layer (6) strongly bonded to the substrate surface (10);

   maintaining the temperature and water vapor concentration within these ranges;

   reacting the gaseous hydrogen/water vapor atmosphere with the specific reactive elements at the substrate surface (10) with oxygen to form a specific reactive element, said barrier layer (2) being strongly bonded to the substrate surface (10), said barrier layer having aluminum oxide (6) at a substrate/barrier layer interface (10).

2. The process of claim 1 wherein the reacting step includes:

   forming $\alpha$Al$_2$O$_3$ (6) directly on the substrate surface (10) in preference to titanium oxide to form an $\alpha$-Al$_2$O$_3$ barrier layer (6);

   reducing titanium atoms from titanium oxide with aluminum and diffusing the titanium atoms outward through the $\alpha$Al$_2$O$_3$ layer (6); and

   oxidizing the titanium atoms that have diffused through the $\alpha$Al$_2$O$_3$ layer (6) to form a Ti$_2$O$_3$ layer (8).
3. The process of claim 2 further including: diffusing other metals in the substrate (4) through the αAl₂O₃ layer (6) into the Ti₂O₃ (8) layer in non-oxidized state.

4. The process of either one of claims 2 or 3 further including:
   oxidizing Ti₂O₃ at a gas/barrier layer interface surface of the Ti₂O₃ layer (8) to form a TiO₂ layer (12) on the Ti₂O₃ layer whereby immiscible layers of TiO₂ (12) and αAl₂O₃ (6) are separated by Ti₂O₃ (8).

5. The process of any one of claims 1-4 further including:
   reacting sulfur at the substrate surface (10) with the hydrogen to form hydrogen sulfide gas; and
   removing the hydrogen sulfide gas from the substrate surface (10).

6. The process of any one of claims 1-5 wherein the heating step includes:
   disassociating oxygen in said water vapor; and
   reacting the disassociated oxygen with said specific reactive elements to form the aluminum (6) and titanium oxide layers (8, 12).

7. The process of claim 6 wherein the reacting step is performed at a subatmospheric pressure.

8. The process of claim 7 wherein the pressure is between about 1x10⁻⁶ to 1x10⁻² kPa.

9. The process of any one of claims 6-8 wherein said high temperature is between 550 and 1100 °C.
10. The process of any one of claims 1-9 wherein the gaseous atmosphere comprises:
   hydrogen at atmospheric pressure that contains less than 750 ppm of water vapor.

11. The process of any one of claims 1-10 wherein the gaseous atmosphere comprises:
   an inert gas at atmospheric pressure that contains less than 750 ppm of water vapor.

12. The process of any one of claims 1-11 wherein the gaseous atmosphere comprises:
   water vapor at a pressure between about $1 \times 10^{-6}$ and $1 \times 10^{-2}$ kPa.

13. The process of any one of claims 1-12 wherein the atmosphere creating step includes:
   heating a region of the substrate surface (10) with a pulsed laser.

14. The process of claim 13 further including:
   controlling an intensity of the laser to hold the substrated below an ablation temperature.

15. The process of claim 14 wherein the laser intensity is below $10^{12}$ Joules/sec$^2$.

16. The process of any one of claims 13-15 wherein the heated region of the substrate is bordered by
   substrate surfaces coated with aluminum oxide.

17. The process of claim 16 wherein the heated region of the substrate is further bordered by a titanium
   oxide layer.
18. The process of any one of claims 1-17 further comprising:
   forming a titanium oxide layer (12) at the barrier layer/gas interface (14).

19. The process of either one of claims 17 and 18 wherein:
   the aluminum oxide layer includes an α-Al₂O₃ layer (6); and
   the titanium oxide layer includes a Ti₂O₃ layer (8).

20. The process of any one of claims 1-19 further including:
   reducing non-specific reactive elements on the surface of said substrate (10) with hydrogen gas.

21. The process of any one of claims 1-20 wherein said titanium aluminide substrate (2) comprises at least 2% aluminum.

22. The process of any one of claims 1-21 wherein said titanium aluminide substrate (2) comprises TiAl₃.

23. The process of any one of claims 1-22 wherein a bond strength between layers is greater than 69,000 kPa.

24. A specific reactive barrier (2) on a titanium and aluminum containing substrate (4), preferably a titanium aluminide substrate, said barrier layer formed by the process of any of claims 1-23.

25. A barrier layer (2) protected titanium aluminide material (10) comprising:
   a titanium aluminide substrate (4);
an aluminum oxide layer (6) bonded to a surface (10) of the titanium aluminide substrate.

26. The barrier layer protected titanium aluminide material (2) of claim 25 further comprising:
   a titanium oxide layer (12) at the barrier layer/gas interface (14).

27. The barrier layer (2) of claim 26 wherein:
   the aluminum oxide layer includes an $\alpha$Al$_2$O$_3$ layer (6); and
   the titanium oxide layer includes a Ti$_2$O$_3$ layer (8).

28. The barrier layer (2) of claim 27 further including:
   a TiO$_2$ layer (12) on the Ti$_2$O$_3$ layer whereby immersible layers of TiO$_2$ (12) and $\alpha$Al$_2$O$_3$ (6) are separated by Ti$_2$O$_3$ (8).

29. The barrier layer (2) of any one of claims 25-28 wherein said titanium aluminide substrate (4) comprises at least 2% aluminum.

30. The barrier layer (2) of any one of claims 25-29 wherein said titanium aluminide substrate (4) comprises TiAl$_3$.

31. The barrier layer (2) of any one of claims 25-30 wherein a bond strength between layers is greater than 69,000 kPa.

32. A process for repairing a damaged barrier layer of any of claims 25-31 comprising:
   maintaining the temperature of the titanium aluminide substrate at a temperature below about 550 °C,
pulsing a laser over the area to be repaired to heat the area to a process temperature between about 550 and 1100 °C, and removing the repaired part from the furnace.
Fig. 1