An enhanced environmental barrier coating for a silicon containing substrate. The enhanced barrier coating may include a bond coat doped with at least one of an alkali metal oxide and an alkali earth metal oxide. The enhanced barrier coating may include a composite mullite bond coat including BSAS and another distinct second phase oxide applied over said surface.
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<table>
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<tr>
<th></th>
<th>BSAS, HfTiO₄, HfO₂, RE₂SiO₅, RE₂Si₂O₇, RE₂O₃, RE₂O₃-ZrO₂, RE₂O₃-HfO₂, combinations thereof</th>
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<td>Chemical Barrier</td>
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<td>Bond Coat</td>
<td>Si, Mullite, BSAS, RE₂SiO₅, RE₂Si₂O₇, RE₂O₃, Ta₂O₅, combinations thereof;</td>
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<tr>
<td></td>
<td>Optionally dope with alkali and alkali earth metal oxides</td>
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<td>Optional bond coat</td>
<td>Silicon, metal silicides, combinations thereof</td>
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RE: Sc, Y, Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu, Sm, Nd, La, combinations thereof;
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<th>Bond coat</th>
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</table>

Figure 10

* CB: Chemical barrier; BC: Bond coat; TC: Top coat
** CB, BC+CB, and CB+TC can be single discrete layer or can form alternating layers with BC and/or TC (BC/BC+CB/BC+TC/TC/BC, etc.), or CB+TC/BC+TC/TC/BC, etc.
*** Compositional grading can be created in BC+CB and/or CB+TC
The present inventions relate generally to an environmental barrier coating system for protecting components exposed to severe environmental and thermal conditions such as the hostile environment present in gas turbine engines. While the present inventions were developed for application in gas turbine engines utilization in other devices is contemplated herein. Designers of gas turbine engines recognize that a limitation to the efficiency and emissions of many gas turbine engines is the temperature capability of metallic components (example, but not limited to blades, vanes, combustor liners) in the engine hot section. Although thermal barrier coatings are used to protect metallic components, thereby allowing the use of higher gas temperatures the metallic components remain a weak link. Silicon-based ceramics, such as SiC/SiC composites and Si₃N₄ ceramics, are prime candidates for hot section components of gas turbine engines. One benefit of silicon-based ceramic engine components is their excellent high temperature mechanical, physical and chemical properties which allow gas turbine engines to operate at higher temperatures than current engines utilizing superalloy components. Higher engine operation temperature translates into significantly reduced emission (pollution) and increased fuel efficiency. However, silicon based ceramic materials suffer from rapid recession in combustion environments due to the volatilization of silica scale by water vapor. This is a significant drawback in the utilization of silicon-based ceramics in gas turbine engines. Therefore, there is a need to identify techniques to limit/prevent the volatilization of silicon-based ceramics in engine operating environments. One technique is to utilize environmental barrier coatings (EBC) that provide the environmental protection for silicon-based ceramics. Current EBCs comprise a bond coat that provides the adherence onto the substrate and a topcoat that provides the environmental protection. The present inventions provide a novel and unobvious environmental barrier coating system.

**SUMMARY**

In one embodiment of the present application, a unique environmental barrier coating is provided to protect a substrate. Other embodiments include unique apparatus, methods, devices, and systems to provide environmental barrier coating protection for a substrate. Further embodiments, forms, features, aspects, benefits, and advantages of the present application shall become apparent from the description and figures provided herewith.

**BRIEF DESCRIPTION OF THE FIGURES**

**FIG. 1** is an illustrative cross sectional view of one embodiment of an environmental barrier coating of the present invention on a substrate.

**FIG. 2** is a cross sectional view of one embodiment of a silicon/mullite+Ta₂O₅-coated SiC substrate.

**FIG. 3** is a cross sectional view of one embodiment of a silicon/mullite-coated SiC substrate.

**FIG. 4** is a cross sectional view of one embodiment of a silicon/mullite+Ta₂O₅-coated SiC substrate after 300 hours with 1 hr cycles at 1400° C.

**FIG. 5** is a view of the silicon/(mullite+BSAS)/BSAS-coated SiC in which BSAS/silica reaction produced low melting glasses after 300 hours at 1400° C.

**FIG. 6** is a cross-section of a silicon/(mullite+Na₂O)/(Sc₂SiO₄+Sc₂O₃) coated SiC substrate after 400 hours at 1316° C. with one hour cycles in a simulated combustion environment (90% H₂O-balance O₂)

**FIG. 7** is a cross section of a silicon/(mullite+Na₂O)/(Sc₂SiO₄+Sc₂O₃) coated SiC substrate.

**FIG. 8** is a cross section of a silicon/mullite/(Sc₂SiO₄+Sc₂O₃) coated SiC substrate.

**FIG. 9** is a chart illustrating various components of environmental barrier coatings.

**FIG. 10** illustrates various embodiments incorporating a chemical barrier into multilayer environmental barrier coating systems.

**FIG. 11** illustrates one embodiment of a single, discreet HISiO₄ chemical barrier between the mullite bond coat and the Yb₂SiO₅ top coat.

**FIG. 12** illustrates one embodiment incorporating HISiO₄ in the bond coat (mullite+Si) via mechanical mixing.

**DETAILED DESCRIPTION OF REPRESENTATIVE EMBODIMENTS**

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is therein intended. Any alterations and further modifications in the described embodiments, and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates. The present invention is directed to an article/component which can withstand an operating environment associated with, but not limited to, the hot section of a gas turbine engine and/or heat exchanger. The article is coated by an environmental barrier coating that in one form resists degradation in various environments including a high temperature water vapor containing combustion environment and/or an environment containing molten salts or CMAS (calcium magnesium aluminum silicate). The present application discloses many things including, but not limited to improving the durability of mullite bond coats by enhancing crack resistance and/or improving adherence. With reference to FIG. 1, there is illustrated an illustrative cross sectional view of an article 10a including one embodiment of an environmental barrier coating 11. The article 10a may be any type of component/part/structure but is preferably a gas turbine engine component/article such as a combustor.
The present invention relates to environmental barrier coatings that provide durability to silicon-containing substrates such as silicon carbide (SiC). These coatings are designed to withstand high-temperature environments, typically over 1300°C, where mullite coatings may degrade due to spallation of the environmental barrier coating. Mullite is a high-temperature insulating material that provides a barrier against chemical reactions and oxidation of the underlying substrate.

The present invention also addresses the durability of the bond coat, which is critical for the overall performance of the environmental barrier coating. Known bond coats, such as mullite, aim to improve the thermal expansion match and chemical compatibility with the topcoat. However, the mullite+BSAS (barium strontium aluminosilicate) bond coat has been developed to enhance these properties, leading to improved durability and oxidation resistance.

By using a bond coat that is designed to more closely match the thermal expansion of the topcoat material, the present invention minimizes coating thermal stress, which is a significant contributor to coating failure. The bond coat is formulated with mullite and BSAS, which together provide a superior barrier against the deleterious effects of high-temperature environments.

In summary, the present invention provides a high-performance environmental barrier coating system that addresses the durability and oxidation resistance challenges associated with silicon-containing substrates, particularly SiC. The innovative bond coat formulation, combining mullite and BSAS, offers enhanced thermal expansion match, improved chemical compatibility, and superior resistance to degradation due to high-temperature thermal exposure.

In the context of the present invention, the bond coat is an integral component that ensures the integrity of the environmental barrier coating system. It is designed to protect the underlying SiC substrate from the corrosive effects of high-temperature environments, thereby extending the service life of the component.

The present invention is significant for applications requiring high-temperature performance, such as aerospace engines, power generation, and other high-temperature industrial processes where silicon carbide and similar materials are utilized.
mullite coating severely delaminated with the formation of thick silica scale after 300 hours at 1400° C (no figure shown), and the (mullite+BSAS)/BSAS-coated SiC (FIG. 5) in which BSAS/silica reaction produced low melting glasses after 300 hours at 1400° C. The low melting glasses in the environmental barrier coatings having (mullite+BSAS) bond coat severely limit the environmental barrier coating life at temperatures over 1300° C. The present application contemplates the bond coat 16 may include Si, mullite, BSAS, RE$_2$SiO$_5$, RE$_2$Si$_2$O$_7$, and combinations thereof. For the readers assistance RE symbolizes the rare earth elements (Sc, Y, Lu, Yb, Tb, Gd, Eu, Sm, Nd, La). Although not as dramatic as Ta$_2$O$_5$, significant improvement in coating durability was observed with the addition of Yb$_2$SiO$_4$.

The modulus of Ta$_2$O$_5$ is between ~110 GPa and ~130 GPa which is lower than that of mullite (~150 GPa), however, the modulus of rare earth silicate (RE$_2$SiO$_5$, RE$_2$Si$_2$O$_7$) is close to that of mullite. This suggests that some factors besides the modulus may be contributing to the improved durability of mullite modified by adding a second phase oxide. One possibility is that the coating simply becomes tougher with the addition of a second phase. The present application includes a durable crack-resistant mullite coating modified by adding a second phase oxide ("composite mullite coating"), preferably low modulus oxides. The second phase oxides include oxides, doped oxides and oxide compounds of transition metals and rare earth elements. Preferred oxides include Ta$_2$O$_5$ and Ta$_2$O$_5$-containing oxides, Nb$_2$O$_5$ and Nb$_2$O$_5$-containing oxides, VO$_2$ and VO$_2$-containing oxides, TiO$_2$ and TiO$_2$-containing oxides, ZrO$_2$ and ZrO$_2$-containing oxides, HfO$_2$ and HfO$_2$-containing oxides, rare earth oxides (including Sc$_2$O$_3$ and Y$_2$O$_3$) and rare earth oxide-containing oxides (including rare earth silicates), NZP family ceramics, and combinations thereof. Si may be added in the second phase to further increase the bonding. The content of the second phase oxide is more than zero wt. % and less than 100 wt. %. In one form the content of the second phase oxide is within a range of 0 wt. % - 50 wt. %. In another form the content of the second phase oxide is within a range of 1 wt. % - 30 wt. %. The second phase oxide may be any combination of oxides listed above. Further, in one form of the present invention the second phase oxide is not defined by BSAS, and in another form of the present application the combination of second phase oxides includes at least one second phase oxide in addition to BSAS. The "composite mullite coating" may be combined with the modification of the mullite coating by doping with alkali and alkali earth metal oxides as set forth in U.S. Provisional Patent Application entitled Alkali and Alkali Earth Metal Oxide Doped Adherent Mullite Coating. Further details regarding the mullite coating doped with alkali and alkali earth metal oxides are provided below. The "composite mullite coating" may be applied on the silicon-based substrate by any suitable method including plasma spraying techniques.

In one form, the present invention provides for substantially higher temperature capability due to the elimination of BSAS second phase from mullite bond coat.

With reference to FIGS. 1 and 6-8, there will be described aspects of the present invention directed to improving the durability of mullite bond coat by improving the adherence. One means to improve the adherence of a coating is by creating an interphase between the coating and the substrate that bond well onto both the coating and the substrate. When mullite-coated silicon-based ceramics are exposed to high temperatures, silica scale grows on the silicon-based ceramics, forming an interphase between the mullite and the substrate. The formation of pure silica scale, however, is detrimental to mullite adherence because it does not bond well onto mullite. Besides the poor adherence onto mullite, silica scale, which is initially amorphous, eventually transforms to cristobalite. This phase transformation is accompanied by a volumetric expansion, leading to cracking of the scale and the deterioration of coating durability.

Introduction of alkali metal or alkali earth metal oxides into silica creates gaps in the continuous network structure in silica. This changes the properties of silica such as reduction in viscosity. A low viscosity silica scale can act like a glue and thus improve the adherence of the mullite bond coat. In one form of the present invention, the viscosity of silica scale was reduced in a controlled manner by doping the mullite bond coat with an alkali or alkali earth metal oxide, which went into the silica scale. As discussed previously, the present application fully contemplates dopping the bond coats discussed above and in reference to FIGS. 2-5 and other bond coats.

In one embodiment a mullite bond coat was doped with a small amount of Li$_2$O or Na$_2$O (less than 5 wt. %). The doped mullite-coated SiC, with or without an additional silicon bond coat, showed significantly improved durability when exposed to a simulated combustion environment (90% H$_2$O-balance O$_2$, 1 hr cycling, 1300-1400° C). The inventor recognizes that too much of Li$_2$O or Na$_2$O in the mullite coating is detrimental to the durability because silica scale with low viscosity will cause accelerated oxygen transport, formation of pores and premature coating spallation. The upper limit of the dopant concentration depends on the temperature and the type of dopant. Smaller amount of dopant is required at higher temperatures because viscosity decreases with increasing temperature. The content of the dopant is more than zero wt. % and less than 10 wt. %. In one form the content of the dopant is within the range of 0.1 wt. % - 5 wt. %.

Since all alkali and alkali earth metal oxides are network-modifying oxides they all have similar effect in reducing the viscosity of silica. Therefore, all common alkali and alkali earth metal oxides, i.e., Li$_2$O, BeO, Na$_2$O, MgO, K$_2$O, CaO, SrO, BaO, and combinations thereof are contemplated as dopant in the present invention. In one form, the dopant may be incorporated in metallic form, i.e., Li, Be, Na, Mg, K, Ca, Sr, and Ba. In another form, Si may be added in the doped mullite bond coat to further increase the bonding.

A silicon bond coat may be applied between the silicon-based substrate and mullite bond coat. Overlay coatings may be applied on top of the doped mullite coating. The doped mullite coating may be used as an intermediate coating.

With reference to FIG. 6, there is illustrated the cross-section of silicon/mullite+Na$_2$O)/SiC after 400 hours at 1316° C. with one hour cycles in a simulated combustion environment (90% H$_2$O-balance O$_2$). The silicon/mullite+Na$_2$O)/SiC coated SiC maintained excellent oxidation resistance, chemically stability and adherence as evidenced by the intact silicon bond coat, the absence of silica scale, and the lack of chemical reaction. On the other hand, the Si/Mullite/Sc$_2$Si$_2$O$_7$+Sc$_2$O$_3$ coated SiC showed extensive oxidation of Si bond coat after the same exposure. FIGS. 7 and 8 compare the cross-section of silicon/mullite+Na$_2$O)/SiC after 300 at 1400° C. with one hour cycles in a simulated combustion environment (90% H$_2$O-balance O$_2$). Again, the silicon/mullite+Na$_2$O)/SiC coated SiC (FIG. 7) maintained excellent oxidation resistance, chemical stability and adherence as evidenced by the intact silicon bond coat, the absence of silica scale and the lack of chemical reaction. This is in contrast to
the silicon/mullite/(SiC=SiO2+SiC) coated SiC (FIG. 8) which showed poor oxidation resistance as evidenced by the loss of the silicon bond coat and the formation of thick porous scale. This data demonstrates the effect of doping with an Alkali or Alkali Earth metal oxide.

Chemical reactions occur at the bond coat/top coat interface in long-term exposures and/or at very high temperatures (>1400° C.). Chemical reactions may alter the chemistry of the bond coat and the top coat, which leads to deleterious physical and mechanical changes of environmental barrier coating layers, such as thermal conductivity, density, modulus, thermal expansion coefficient, etc. Therefore, it is often desirable to limit the deleterious chemical reactions between the layers to maximize the environmental barrier coating life. As discussed previously the environmental barrier coating may be considered to include bond coat, top coat and other material coats/layers utilized to protect the substrate. For example, some rare earth oxide components such as yttria (one key stabilizer for zirconia and hafnia) readily react with mullite forming a low melting (<1400° C.) products, which can significantly alter the coating properties and shorten the life. Many current environmental barrier coatings having stabilized zirconia or hafnia develop a large coefficient of thermal expansion mismatch strain, limiting the T/EBC life by causing cracking and delamination.

Extensive chemical compatibility studies at 1500° C. showed that HfSiO4 has excellent chemical compatibility with mullite, BSAS, rare earth silicate, rare earth oxide-stabilized zirconia, and rare earth oxide-stabilized hafnia. Some rare earth silicates (RE2Si2O5 or RE2Si2O7; RE=Yb, Lu, Sc) also show excellent chemical compatibility with mullite, BSAS, rare earth oxide-stabilized zirconia, and rare earth oxide-stabilized hafnia. Besides the chemical compatibility, HfSiO4, RE2SiO5, and RE2Si2O7 have good coefficient of thermal expansion match with the mullite-based bond coat and SiC or Si3N4 substrate, making them excellent candidates for the chemical barrier. A low modulus chemical barrier can be a compliant layer as well relaxing the coefficient of thermal expansion mismatch strain. FIG. 9 illustrates various components of environmental barrier coatings. The top coat can be BSAS, HTfIO4, HfO2, RE2SiO5, RE2Si2O7, RE3O5, RE2O5-ZrO2, RE2O5-HfO2, and combinations thereof, where RE=Sc, Y, Lu, Yb, Tb, Er, Ho, Dy, Tm, Gd, Eu, Sm, Nd, La. The present application further contemplates the combination of the RE materials. In one form the total content of RE2O5 in RE2O5-ZrO2 and RE2O5-HfO2 is more than 1 mol % and less than 20 mol %. In a preferred form the content of RE2O5 in RE2O5-ZrO2 and RE2O5-HfO2 is 4 mol % - 10 mol %.

The chemical barrier can be incorporated as a discrete layer, a graded layer, a mechanical mixture with the bond coat and/or the top coat, alternating multilayers with the bond coat and/or the top coat, or combinations thereof. FIG. 10 shows various examples of incorporating the chemical barrier into multilayer environmental barrier coating systems. The graded layer and alternating layers should help spread out the coefficient of thermal expansion mismatch strain in the case of a high coefficient of thermal expansion top coat (stabilized zirconia and hafnia). Alternating multilayers should help toughen the environmental barrier coating by creating a composite layer.

FIG. 11 shows an example of a single, discrete HfSiO4 chemical barrier between the mullite bond coat and the Yb2Si2O6 top coat, and FIG. 12 shows an example of incorporating HfSiO4 in the bond coat (mullite+Si) via mechanical mixing. The environmental barrier coating maintained excellent chemical, environmental, chemical and mechanical durability in simulated combustion environments (FIG. 11: 1450° C., 1 hr eycles, 100 hr, 90% H2O-bal. O2; FIG. 12: 1430° C., 1 hr cycles, 100 hr, 90% H2O-bal. O2). The benefits of the chemical barrier in these examples are as follows. In the case of FIG. 11, the chemical barrier makes the coating more robust by preventing chemical reaction and/or delamination at the top coat/bond coat interface in very high temperature exposures (≥1450° C.). In the case of FIG. 12, the HfSiO4 component prevents the deleterious chemical reaction between mullite and the additives (rare earth oxides) in Si3N4. The mullite bond coat readily delaminates without the HfSiO4 component.

One form of the present application contemplates an apparatus comprising: a silicon based ceramic substrate; and, a composite mullite coating applied over at least a portion of the ceramic substrate. Another aspect of the present application contemplates the composite coating includes mullite and Ta2O5. Another aspect of the present application contemplates the composite coating includes a second phase oxide. Yet another aspect of the present application contemplates the oxide includes at least one of Ta2O5 and Ta2O5-containing oxides, Nb2O5 and Nb2O5-containing oxides, VO2 and VO2-containing oxides, TiO2 and TiO2-containing oxides, ZrO2 and ZrO2-containing oxides, HfO2 and HfO2-containing oxides, rare earth oxides, and rare earth oxide-containing oxides (including rare earth silicates), NZP ceramics.

Another form of the present application contemplates a gas turbine engine component, comprising: a silicon based ceramic component; and, coating means applied over at least a portion of said structure for preventing the volatilization of said ceramic component.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic structure; and, a mullite bond coat doped with an alkali metal or alkali earth metal oxide applied over at least a portion of said ceramic structure.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic component; and, a mullite bond coat doped with dopant means for reducing the viscosity of silica. Another aspect of the present application contemplates the dopant means is defined by an alkali metal or alkali earth metal oxide. Yet another aspect of the present application contemplates the dopant means is defined by a combination of alkali metal and/or alkali earth metal oxides. Yet another aspect of the present application contemplates the addition of a silicon bond coat applied on at least a portion of the ceramic structure, and the mullite bond coat is applied over said silicon bond coat.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic component; and, a mullite bond coat doped with dopant means for reducing the viscosity of silica. Another aspect of the present application contemplates the dopant means is defined by an alkali metal or alkali earth metal oxide. Yet another aspect of the present application contemplates the dopant means is defined by a combination of alkali metal and/or alkali earth metal oxides. Yet another aspect of the present application contemplates the addition of a silicon bond coat applied on at least a portion of the ceramic structure, and the mullite bond coat is applied over said silicon bond coat.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic substrate; a mullite bond coat; and a low modulus chemical barrier applied over said bond coat; and a topcoat applied over said chemical barrier.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic substrate; a mullite bond coat; and a low modulus chemical barrier applied over said bond coat; and a topcoat applied over said chemical barrier.

Another form of the present application contemplates an apparatus comprising: a silicon based ceramic substrate; a mullite bond coat; and a low modulus chemical barrier applied over said bond coat; and a topcoat applied over said chemical barrier.
a portion of the substrate; and introducing at least one of an alkali metal oxide and an alkali earth metal oxide into the silica scale. Another aspect of the present application contemplates wherein in said introducing the at least one of an alkali metal oxide and an alkali earth metal oxide come from the bond coat. Another aspect of the present application contemplates the content of the at least one of an alkali metal oxide and an alkali earth metal oxide in the bond coat is more than zero wt. % and less than 10 wt. %. Another aspect of the present application contemplates that the content of the at least one of an alkali metal oxide and an alkali earth metal oxide in the bond coat is within the range of 0.1 wt. % to 5 wt. %. Another aspect of the present application contemplates that the bond coat includes a dopant in a metallic form, wherein the dopant is selected from the group consisting of Li, Be, Na, Mg, K, Cu, Sr, and Ba and combinations thereof. Another aspect of the present application contemplates that in said introducing the at least one alkali metal oxide and an alkali earth metal oxide is selected from the group consisting of Li2O, Na2O, MgO, K2O, CaO, SrO, BaO and combinations thereof. Another aspect of the present application contemplates forming a second bond coat between the substrate and the bond coat, wherein the second bond coat is selected from the group consisting of silicon, metal silicides and combinations thereof. Another aspect of the present application contemplates forming gaps in the continuous network structure of the silica. Another aspect of the present application contemplates adhering the bond coat to the substrate. Another aspect of the present application contemplates adhering the bond coat to the substrate; wherein said creating includes the dopant. Another aspect of the present application contemplates that the silicon containing substrate is selected from the group consisting of HfSiO4, RE2SiO5, and RE2Si2O11, RE2O3, RE2O3·ZrO2, RE2O3·HfO2, and combinations thereof. Another aspect of the present application contemplates the introduction of at least one of an alkali metal oxide and an alkali earth metal oxide into the silica scale; which further includes introducing at least one alkali metal oxide or alkali earth metal oxide into the silica scale. Another aspect of the present application contemplates adhering the bond coat to the substrate; wherein said creating includes the dopant. Another aspect of the present application contemplates that the silicon containing substrate is defined by a carbon fiber reinforced silicon carbide matrix composite. Another aspect of the present application contemplates adhering the bond coat to the substrate; wherein said creating includes the dopant. Another aspect of the present application contemplates doping the bond coat with a dopant having a content greater than 0.0 wt % and less than 10 wt. %. Another aspect of the present application contemplates that the dopant is selected from the group consisting of alkali metal oxide, alkali earth metal oxide, Li, Be, Na, Mg, K, Ca, Sr, and Ba. Another aspect of the present application contemplates that the dopant is selected from the group consisting of Li2O, BeO, Na2O, MgO, K2O, CaO, SrO, BaO and combinations thereof. Another aspect of the present application contemplates that the dopant is within a range between 0.0 wt. % and 10.0 wt. %. Another aspect of the present application contemplates doping the bond coat with a dopant having a content greater than 0.0 wt % and less than 10 wt. %. Another aspect of the present application contemplates that the dopant is selected from the group consisting of alkali metal oxide, alkali earth metal oxide, Li, Be, Na, Mg, K, Ca, Sr, and Ba. Another aspect of the present application contemplates that the dopant is selected from the group consisting of Li2O, BeO, Na2O, MgO, K2O, CaO, SrO, BaO and combinations thereof. Another aspect of the present application contemplates that the dopant is selected from the group consisting of alkali metal oxide, alkali earth metal oxide, Li, Be, Na, Mg, K, Ca, Sr, and Ba.
plates that the second phase oxide is selected from the group consisting of Nb$_2$O$_5$-containing oxides, V$_2$O$_5$-containing oxides, RE$_2$O$_3$, RE$_2$O$_3$ ZrO$_2$, RE$_2$O$_3$ HfO$_2$, and combinations thereof. Another aspect of the present application contemplates that the bond coat is adhered to the substrate; and which further includes a top coat over the bond coat. Another aspect of the present application contemplates that the top coat is selected from the group consisting of BSAS, HfTiO$_4$, HfO$_2$, RE$_2$SiO$_4$, RE$_2$Si$_2$O$_7$, RE$_2$O$_3$, RE$_2$O$_4$—ZrO$_2$, RE$_2$O$_4$—HfO$_2$, and combinations thereof. Another aspect of the present application contemplates a silica scale over the bond coat. Another aspect of the present application contemplates applying a chemical barrier between the top coat and the bond coat. Another aspect of the present application contemplates that the chemical barrier is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_4$, and RE$_2$Si$_2$O$_7$, and combinations thereof. Another aspect of the present application contemplates that the bond coat is adhered to the substrate; which further includes a top coat over said bond coat; and wherein the content of the second phase oxide is within the range of 1 wt.% to 30 wt.%.

Another aspect of the present application contemplates that the bond coat is adhered to the substrate; and which further includes a top coat over the bond coat. Another aspect of the present application contemplates that the top coat is selected from the group consisting of BSAS, HfTiO$_4$, HfO$_2$, RE$_2$SiO$_4$, RE$_2$Si$_2$O$_7$, RE$_2$O$_3$, RE$_2$O$_4$—ZrO$_2$, RE$_2$O$_4$—HfO$_2$, and combinations thereof. Another aspect of the present application contemplates applying a chemical barrier between the top coat and the bond coat. Another aspect of the present application contemplates that the chemical barrier is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_4$, and RE$_2$Si$_2$O$_7$, and combinations thereof. Another aspect of the present application contemplates that the bond coat is adhered to the substrate; which further includes a top coat over said bond coat; and wherein the content of the second phase oxide is within the range of 1 wt.% to 30 wt.%.

Another aspect of the present application contemplates that the bond coat is adhered to the substrate; which further includes a top coat over the bond coat. Another aspect of the present application contemplates that the top coat is selected from the group consisting of BSAS, HfTiO$_4$, HfO$_2$, RE$_2$SiO$_4$, RE$_2$Si$_2$O$_7$, RE$_2$O$_3$, RE$_2$O$_4$—ZrO$_2$, RE$_2$O$_4$—HfO$_2$, and combinations thereof. Another aspect of the present application contemplates applying a chemical barrier between the top coat and the bond coat. Another aspect of the present application contemplates that the chemical barrier is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_4$, and RE$_2$Si$_2$O$_7$, and combinations thereof. Another aspect of the present application contemplates a silica scale over the bond coat. Another aspect of the present application contemplates applying a chemical barrier between the top coat and the bond coat. Another aspect of the present application contemplates that the chemical barrier is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_4$, and RE$_2$Si$_2$O$_7$, and combinations thereof. Another aspect of the present application contemplates that the bond coat is adhered to the substrate; which further includes a top coat over said bond coat; and wherein the content of the second phase oxide is within the range of 1 wt.% to 30 wt.%.

Another form of the present application contemplates an apparatus comprising: a silicon containing substrate having a surface; and a composite mullite bond coat applied over said surface, said bond coat including a second phase oxide and doped with an alkali material or an alkali earth material. Another aspect of the present application contemplates that the apparatus is a gas turbine engine component. Another aspect of present application contemplates that the gas turbine engine component is selected from the group consisting of a combustor liner, blade, vane and blade track. Another aspect of the present application contemplates that the bond coat is adhered to the substrate. Another aspect of the present application contemplates that the bond coat is adhered to the substrate; which further includes a top coat over said bond coat; and wherein the content of the second phase oxide is within the range of 1 wt.% to 30 wt.%.
distinct second phase oxide applied over said surface. Another aspect of the present application contemplates that the bond coat is doped with at least one of an alkali metal oxide and an alkali earth metal oxide. Another aspect of the present application contemplates that the bond coat is doped with both an alkali metal oxide and an alkali earth metal oxide. Another aspect of the present application contemplates including a top coat over said bond coat. Another aspect of the present application contemplates that the top coat is selected from the group consisting of BSAS, HfSiO$_4$, HfO$_2$, RE$_2$SiO$_5$, RE$_2$Si$_2$O$_7$, RE$_2$O$_3$, RE$_2$O$_3$—ZrO$_2$, RE$_2$O$_3$—HfO$_2$, and combinations thereof. Another aspect of the present application contemplates applying a chemical barrier between the top coat and the bond coat. Another aspect of the present application contemplates that the chemical barrier is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_5$, and RE$_2$Si$_2$O$_7$ and combinations thereof.

Another form of the present application contemplates an apparatus comprising: a substrate having a surface; and a composite mullite bond coat applied over said surface, said bond coat including a second phase oxide and doped with an alkali material or an alkali earth material.

Another form of the present application contemplates an apparatus comprising: a substrate having a surface; and a mullite bond coat doped with an alkali material or an alkali earth material and applied over at least a portion of said surface.

Another form of the present application contemplates an apparatus comprising: a substrate having a surface; and a composite mullite bond coat including a second phase oxide other than BSAS applied over said surface.

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered illustrative and not restrictive in character, it being understood that only selected embodiments have been shown and described and that all changes, equivalents, and modifications that come within the scope of the inventions described herein or defined by the following claims are desired to be protected. Any experiments, experimental examples, or experimental results provided herein are intended to be illustrative of the present invention and should not be construed to limit or restrict the invention scope. Further, any theory, mechanism of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to limit the present invention in any way to such theory, mechanism of operation, proof, or finding. In reading the claims, words such as "a", "an", "at least on", and "at least a portion" are not intended to limit the claims to only one item unless specifically stated to the contrary. Further, when the language "at least a portion" and/or "a portion" is used, the claims may include a portion and/or the entire item unless specifically stated to the contrary. Any patent application, publication or patent listed in this document is incorporated herein in its entirety.

What is claimed is:
1. An article comprising: a silicon containing substrate having a surface; a composite mullite bond coat including a mullite phase, a second oxide phase other than BSAS, and a dopant material over the surface, wherein the dopant material comprises at least one of an alkali metal or an alkali earth metal oxide, and wherein the second oxide phase comprises at least one of a transition metal oxide, a rare earth oxide, a rare earth silicate, or a NZP ceramic; and a silica scale between the substrate and the composite mullite bond coat and having gaps in a continuous network structure of the silica scale, wherein the silica scale includes the at least one of an alkali metal or an alkali earth metal oxide.
2. The article of claim 1, wherein the second oxide phase comprises an oxide having a Young's modulus lower than about 150 GPa.
3. The article of claim 1, wherein the composite mullite bond coat comprises the second oxide phase within the range of more than 0 wt. % and up to 50 wt. %.
4. The article of claim 1, wherein the composite mullite bond coat comprises the second oxide phase within the range of 1 wt. % to 30 wt. %.
5. The article of claim 1, wherein the composite mullite bond coat is doped with between 0.1 wt. % and 5 wt. % of the alkali metal oxide.
6. The article of claim 1, wherein the composite mullite bond coat is adhered to the substrate.
7. The article of claim 1, further comprising a second bond coat between the substrate and the composite mullite bond coat, wherein the second bond coat is selected from the group consisting of silicon, metal silicides, and combinations thereof.
8. The article of claim 1, further comprising a top coat over the composite mullite bond coat.
9. The article of claim 8, wherein the top coat is selected from the group consisting of BSAS, HfSiO$_4$, HfO$_2$, RE$_2$SiO$_5$, RE$_2$Si$_2$O$_7$, RE$_2$O$_3$, RE$_2$O$_3$—ZrO$_2$, RE$_2$O$_3$—HfO$_2$, and combinations thereof.
10. The article of claim 9, wherein the content of RE$_2$O$_3$ in RE$_2$O$_3$—ZrO$_2$ and RE$_2$O$_3$—HfO$_2$ is within the range of 4 mol % to 10 mol %.
11. The article of claim 8, further comprising a chemical barrier layer between the top coat and the composite mullite bond coat.
12. The article of claim 11, wherein the chemical barrier layer is selected from the group consisting of HfSiO$_4$, RE$_2$SiO$_5$, RE$_2$Si$_2$O$_7$, and combinations thereof.
13. The article of claim 1, wherein the composite mullite bond coat is adhered to the substrate; further comprising a top coat over the composite mullite bond coat; and wherein the composite mullite bond coat comprises between 1 wt. % and 30 wt. % of the second oxide phase.
14. The article of claim 1, wherein the article is a gas turbine engine component.
15. The article of claim 14, wherein the gas turbine engine component is selected from the group consisting of a combustor liner, blade, vane and blade track.
16. The article of claim 1, wherein the composite mullite bond coat is further doped with an alkaline earth metal oxide.
17. The article of claim 1, wherein the composite mullite bond coat further includes silicon.