A barrier layer for a silicon containing substrate which inhibits the formation of gaseous species of silicon when exposed to a high temperature aqueous environment comprises a barium-strontium alumino silicate.
**FIG. 1**

**FIG. 4**
FIG. 3
The present invention relates to an article comprising a substrate containing silicon and a barrier layer which functions as a protective environmental/thermal barrier coating and, more particularly, a barrier layer which inhibits the formation of gaseous species of Si, particularly Si(OH), when the article is exposed to a high temperature, aqueous (water and/or steam) environment.

Ceramic materials containing silicon and metal alloys containing silicon have been proposed for structures used in high temperature applications as, for example, gas turbine engines, heat exchangers, internal combustion engines, and the like. A particular useful application for these materials is for use in gas turbine engines which operate at high temperatures in aqueous environments. It has been found that these silicon containing substrates can recede and lose mass as a result of a formation volatile Si species, particularly Si(OH), and SiO, when exposed to high temperature, aqueous environments. For example, silicon carbide when exposed to a lean fuel environment of approximately 1 ATM pressure of water vapor at 1200° C. will exhibit weight loss and recession at a rate of approximately 6 mils per 1000 hrs.

It is believed that the process involves oxidation of the silicon carbide to form silica on the surface of the silicon carbide followed by reaction of the silica with steam to form volatile species of silicon such as Si(OH). Subsequently, it would be highly desirable to provide an external barrier coating for silicon containing substrates which would inhibit the formation of volatile silicon species, Si(OH), and SiO, and thereby reduce recession and mass loss.

Accordingly, it is the principle object of the present invention to provide an article comprising a silicon containing substrate with a barrier layer which inhibits the formation of gaseous species of Si, particularly Si(OH), when the article is exposed to a high temperature, aqueous environment.

A second objective of this invention is to provide an article comprising a substrate with a barrier layer providing thermal protection, such layer closely matching the thermal expansion of the substrate.

It is a further object of the present invention to provide a method for producing an article as aforesaid.

SUMMARY OF THE INVENTION

The present invention relates to an article comprising a silicon containing substrate having a barrier layer on the substrate, wherein the barrier layer functions to both inhibit the formation of undesirable gaseous species of silicon when the article is exposed to a high temperature, aqueous environment and to provide thermal protection. By high temperatures is meant the temperature at which the Si in the substrate forms Si(III), and/or SiO in an aqueous environment. By aqueous environment is meant a water and/or steam environment. The silicon containing composite is preferably a ceramic or metal alloy containing silicon. The external barrier layer is characterized by a coefficient of thermal expansion which is within plus or minus 3.0 ppm per degree centigrade of the coefficient of expansion of the silicon containing substrate. The preferred barrier layer in accordance with the present invention is a barium alumino-silicate and, preferably, a barium-alkaline earth aluminosilicate wherein the alkaline earth metal is ideally strontium. In a preferred embodiment of the present invention the article can include one or more intermediate layers between the silicon based substrate and the barrier layer. The intermediate layer(s) serves to provide enhanced adherence between the barrier layer and the substrate and/or to prevent reactions between the barrier layer and the substrate.

The invention further relates to a method for producing an article comprising a silicon containing substrate and a barrier layer which inhibits the formation of gaseous species of silicon and/or provides thermal protection when the article is exposed to a high temperature, aqueous environment as defined above.

Further objects and advantages of the present invention will appear hereinafter from the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the stability of the barrier layer of the present invention with respect to recession and mass loss;

FIG. 2 is a photomicrograph through a sample of the barrier layer of the present invention on a silicon carbide substrate;

FIG. 3 is a photomicrograph of a sample of the barrier layer of the present invention applied to an intermediate layer on a silicon carbide substrate; and

FIG. 4 demonstrates the effect of three specimens of the barrier layer of the present invention on weight loss in high temperature, aqueous environments.

DETAILED DESCRIPTION

The present invention relates to an article comprising a silicon containing substrate and a barrier layer, wherein the barrier layer inhibits the formation of gaseous species of silicon when the article is exposed to a high temperature, aqueous environment. The invention also relates to a method for producing the aforesaid article. In addition, it should be appreciated that while the barrier is particularly directed to an environmental barrier layer, the barrier layer also functions as a thermal barrier layer and thus the present invention broadly encompasses the use of environmental/thermal barrier layers on silicon containing substrates and on substrates having comparable thermal expansion coefficients.

According to the present invention, the silicon containing substrate may be a silicon containing ceramic substrate or a silicon containing metal alloy. In a preferred embodiment, the silicon containing substrate is a silicon containing ceramic material as, for example, silicon carbide, silicon nitride, silicon carbon nitride, silicon oxynitride and silicon aluminum oxynitride. In accordance with a particular embodiment of the present invention, the silicon containing ceramic substrate comprises a silicon containing matrix with reinforcing such as fibers, particles, and the like and, more particularly, a silicon based matrix which is fiber-reinforced. Particularly suitable ceramic substrates are a silicon carbide coated silicon carbide fiber-reinforced silicon carbide particle and silicon matrix, a carbon fiber-reinforced silicon carbide matrix and a silicon carbide fiber-reinforced silicon nitride matrix. Particularly useful silicon-metal alloys for
Accordingly, it is preferred that the barrier layer comprises multilayer-strontium alumino-silicate, multilayer-yttrium silicate, or multilayer-calcium alumino-silicate in an amount of between about 40 to 80 wt. % multilayer and between about 20 to 60 wt. % barium strontium alumino-silicate or yttrium silicate or calcium alumino-silicate. The thickness of the intermediate layer is typical to those described above with regard to the barrier layer and the intermediate layer may likewise be disposed in any manner known in the prior art, however, preferably by thermal spraying as described hereinafter.

In addition to the intermediate layer, a bond layer may be provided between the silicon containing substrate and the intermediate layer. A suitable bond layer includes silicon metal in a thickness of 3 to 6 mils. Alternatively, the silicon containing substrate may be pre-oxidized to provide a SiO₂ bond layer prior to application of the intermediate layer.

The method of the present invention comprises providing a silicon containing substrate and applying a barrier layer wherein the barrier layer inhibits the formation of gaseous species of silicon when the article is exposed to a high temperature, aqueous environment. In accordance with the present invention it is preferred that the barrier layer be applied by thermal spraying. It has been found that the barrier layer should be thermal sprayed at a temperature of between about 870°C to 1200°C in order to help equilibrate the as-sprayed, splat quenched, microstructure and to provide a means to manage stresses which control delamination. When the article being prepared in accordance with the method of the present invention is a silicon containing ceramic with a barium strontium alumino-silicate barrier layer, it is preferred that the barium strontium alumino-silicate barrier layer have celsian crystallographic structure in an amount of at least 50% by volume in the barrier layer. The formation of the celsian crystallographic structure insures compatibility between the coefficient of thermal expansion of the silicon containing ceramic and the barium strontium alumino-silicate barrier layer as described above.

The silicon containing substrate should be cleaned prior to application of the barrier layer to remove substrate fabrication contamination. It is preferred that the silicon based substrate be subjected to a grit blasting step prior to application of the barrier layer. The grit blasting step must be carried out carefully in order to avoid damage to the surface of the silicon-containing substrate such as silicon carbide fiber reinforced composite. It has been found that the particles used for the grit blasting should be hard enough to remove the undesired contamination but not as hard as the substrate material to prevent erosive removal of the substrate. Further, the particles must be small to prevent impact damage to the substrate. When processing an article comprising a silicon carbide ceramic composite substrate, it has been found that the grit blasting should be carried out with Al₄O₅ particles, preferably of a particle size of ≤ 30 microns and, preferably, at a velocity of about 150 to 200 m/sec. In addition to the foregoing, it may be particularly useful to preoxidize the silicon based substrate prior to application of the intermediate and/or barrier layer in order to improve adherence. It has been found that bond layers of between 100 nanometers to 2000 nanometers are preferred. SiO₂ bond layers of the desired thickness can be achieved by preoxidizing the silicon-carbide substrate at a temperature of between 800°C to 1200°C for about 15 minutes to 100 hours.

The silicon bond layer may be applied directly to the grit blasted surface by thermal spraying at approximately 870°C to a thickness of 3 to 6 mils.
Intermediate layers may be applied between the substrate and/or bond layer and the barrier layer or between the bond layer and barrier layer by thermal spraying in the same manner described above with respect to the barrier layer. As noted above, the preferred intermediate layers include mullite, mullite-barium strontium aluminosilicate, mullite-yttrium silicate, and mullite-calcium aluminosilicate.

After application of the desired layers to the silicon-based substrate material, the article is subjected to a heat treatment step in order to provide stress relief to the thermal sprayed structure, to promote bonding between the sprayed powder particles and between the layers and the substrate, and to develop the celsian phase in the BSAS barrier layer which is essentially amorphous in the as sprayed condition. The heat treatment step is carried out at a temperature of about 1250°C for about 24 hours.

The advantages of the article of the present invention will become clear from consideration of the following examples.

EXAMPLE 1

FIG. 1 shows a comparison of a hot pressed bulk specimen of BSAS, of composition 0.75 BaO.0.25 SrO.AI₂O₃.2 SiO₂, in comparison to silicon carbide thermal cycle tested 250 cycles between room temperature and 1200°C in a simulated combustion environment of high steam, lean fuel conditions. The results show 8 mg/cm² weight loss for the silicon carbide while the BSAS gains a very small amount of weight ~0.4 mg/cm². The results show that silicon carbide is not stable to this environment and that the BSAS system is much more stable.

EXAMPLE 2

FIG. 2 is a cross section of a 4 mil thick BSAS of composition 0.75 BaO.0.25 SrO.AI₂O₃.2 SiO₂ coating on SiC composite. The BSAS was thermal sprayed onto the silicon carbide composite using the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma torch</td>
<td>Metco 3M</td>
</tr>
<tr>
<td>Nozzle</td>
<td>GH</td>
</tr>
<tr>
<td>Anode</td>
<td>std.</td>
</tr>
<tr>
<td>Powder port</td>
<td>Metco #2</td>
</tr>
<tr>
<td>Primary gas</td>
<td>Ar@80 Metco gage</td>
</tr>
<tr>
<td>Secondary gas</td>
<td>H₂O@ Metco gage</td>
</tr>
<tr>
<td>Substrate temp.</td>
<td>850°C</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Ar@37 Metco gage</td>
</tr>
<tr>
<td>Powder feed</td>
<td>15 to 25 gpm</td>
</tr>
</tbody>
</table>

Prior to coating the substrate was cleaned by grit blasting with 27 micron alumina particles at an impact velocity of 150 to 200 mps. As can be seen from FIG. 2, the invention results in an excellent barrier layer structure.

EXAMPLE 3

FIG. 3 is a cross sectional view of a BSAS of composition 0.75 BaO.0.25 SrO.AI₂O₃.2 SiO₂, barrier layer on silicon carbide composite. The coating was fabricated using the following parameters.

Prior to coating the substrate was cleaned by grit blasting with 27 micron alumina particles at an impact velocity of 150 to 200 mps. As can be seen from FIG. 3, the invention results in an excellent barrier layer structure.

EXAMPLE 4

The results are shown in FIG. 4 below which shows the effectiveness of the barrier layer of the present invention.

EXAMPLE 5

The coefficient of thermal expansion (CTE) was measured for BSAS systems of 0.75 BaO.0.25 SrO.AI₂O₃.2 SiO₂.
having different celsian contents. Celsian content was deter-
mined by x-ray analysis of hot pressed coupons of BSAS.
The celsian content affected the CTE as seen below.

<table>
<thead>
<tr>
<th>% Celsian Content</th>
<th>CTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>8.1</td>
</tr>
<tr>
<td>25</td>
<td>7.4</td>
</tr>
<tr>
<td>95</td>
<td>5.2</td>
</tr>
</tbody>
</table>

This invention may be embodied in other forms or carried
out in other ways without departing from the spirit or
essential characteristics thereof. The present embodiment
is therefore to be considered as in all respects illustrative
and not restrictive, the scope of the invention being indicated by
the appended claims, and all changes which come within the
meaning and range of equivalency are intended to be
embraced therein.

What is claimed is:

1. An article comprising:
a substrate comprising silicon; and
a gaseous species of Si formation inhibiting barrier layer,
wherein the barrier layer is selected from the group
consisting of (a) barium oxide, (b) barium alumino-
silicate, (c) barium strontium aluminosilicate, (d) from
about 0.00 to 1.00 mole BaO, from about 0.00
to 1.00 mole SrO, about 1.0 mole Al₂O₃ and about 2.00
mole SiO₂ wherein the total of BaO and SrO is about
1.00 mole and (e) from about 0.00 to 1.00 mole BaO,
from about 0.00 to 1.00 mole of an oxide of a second
alkaline earth metal, about 1.00 mole Al₂O₃ and about
2.00 mole SiO₂ wherein BaO plus the other alkaline
earth metal oxide total 1 mole wherein the barrier layer
has a crystallographic structure which is at least 50%
by volume celsian and inhibits the formation of a
gaseous species of Si when the article is exposed to a
high temperature, aqueous environment.

2. An article according to claim 1 wherein the substrate
is selected from the group consisting of a silicon containing
ceramic and metal alloys containing silicon.

3. An article according to claim 2 wherein the substrate
is a silicon containing ceramic selected from the group
consisting of silicon carbide, silicon nitride, and silicon aluminum
nitride.

4. An article according to claim 2 wherein the substrate
is a composite comprising a silicon based matrix and a rein-
forcing particle.

5. An article according to claim 4 wherein said substrate
is selected from the group consisting of silicon carbide
fiber-reinforced silicon carbide matrix, carbon fiber-
reinforced silicon carbide matrix and silicon carbide fiber-
reinforced silicon nitride.

6. An article according to claim 2 wherein said substrate
is a silicon containing metal alloy selected from the group
consisting of molybdenum-silicon alloys, niobium silicon
alloys, iron-silicon alloys, and iron-nickel-silicon based
alloys.

7. An article according to claim 1 wherein the barrier layer
comprises from about 0.10 mole to about 0.90 mole BaO and
from about 0.10 mole to about 0.90 mole SrO.

8. An article according to claim 1 wherein the barrier layer
comprises from about 0.25 mole to about 0.75 mole BaO and
from about 0.25 mole to about 0.75 mole SrO.

9. An article according to claim 1 wherein the barrier layer
comprises about 0.75 mole BaO and about 0.25 mole SrO.

10. An article according to claim 1 wherein the barrier layer
comprises from about 0.10 mole to about 0.90 mole
BaO and from about 0.10 mole to about 0.90 mole of a
second alkaline earth oxide.

11. An article according to claim 12 wherein the barrier layer
comprises from about 0.25 mole to about 0.75 mole
BaO and from about 0.25 mole to about 0.75 mole of a
second alkaline earth oxide.

12. An article according to claim 1 wherein the barrier layer
comprises about 0.75 mole BaO and about 0.25 mole of a
second alkaline earth oxide.

13. An article according to claim 1 wherein the coefficient
of thermal expansion of the barrier layer is within ±0.3
ppm/°C, the coefficient of thermal expansion of the sub-
strate.

14. An article according to claim 1 wherein the coefficient
of thermal expansion of the barrier layer is within ±0.5
ppm/°C, the coefficient of thermal expansion of the sub-
strate.

15. An article according to claim 1 wherein the barrier layer
has a thickness of ±0.5 mils (0.0005 inch).

16. An article according to claim 1 including an interme-
diate layer between the substrate and the barrier layer.

17. An article according to claim 16 wherein said interme-
diate layer is selected from the group consisting of SiO₂,
mullite, mullite-barium strontium aluminosilicate, mullite-
ytrium silicate, mullite-calcium aluminosilicate, and silicon
metal.

18. An article according to claim 16 wherein said interme-
diate layer is selected from the group consisting of
mullite, barium strontium aluminosilicate, mullite-yttrium
silicate, calcium aluminosilicate and mixtures thereof.

19. An article according to claim 18 wherein said interme-
diate layer comprises mullite.

20. An article according to claim 18 wherein said interme-
diate layer comprises from about 40 to 80 wt. % mullite
and from about 60 to 20 wt. % barium strontium alumi-
osilicate.

21. An article according to claim 18 wherein said interme-
diate layer comprises from about 40 to 80 wt. % mullite
and from about 60 to 20 wt. % yttrium silicate.

22. An article according to claim 18 wherein said interme-
diate layer comprises from about 40 to 80 wt. % mullite
and from about 60 to 20 wt. % calcium aluminosilicate.

23. An article according to claim 16 including a bond layer
between the substrate and the intermediate layer.

24. An article according to claim 23 wherein the bond
layer is silicon metal or SiO₂.

25. An article according to claim 16 wherein the interme-
diate layer has a thickness of ±0.5 mils (0.0005 inch).

26. An article according to claim 1 wherein the barrier
layer has a thickness of between about 3 to 30 mils.

27. An article according to claim 1 wherein the barrier
layer has a thickness of between about 3 to 5 mils.

28. An article according to claim 16 wherein the interme-
diate layer has a thickness of 3 to 30 mils.

29. An article according to claim 16 wherein the interme-
diate layer has a thickness of 3 to 5 mils.

30. An article according to claim 23 wherein the bond
layer has a thickness of between about 3 to 6 mils.

31. An article comprising:
a substrate comprising silicon;
a gaseous species of Si formation inhibiting barrier layer,
wherein the barrier layer inhibits the formation of a
gaseous species of Si when the article is exposed to a
high temperature, aqueous environment; and
an intermediate layer between the substrate and the barrier
layer wherein the intermediate layer is selected from the
group consisting of SiO₂, mullite, mullite-barium
strontium aluminosilicate, mullite-yttrium silicate, mullite-calcium aluminosilicate, barium strontium aluminosilicate, calcium aluminosilicate, and silicon metal.

32. An article according to claim 31 wherein said intermediate layer comprises mullite.

33. An article according to claim 31 wherein said intermediate layer comprises from about 40 to 80 wt. % mullite and from about 60 to 20 wt. % barium strontium aluminosilicate.

34. An article according to claim 31 wherein said intermediate layer comprises from about 40 to 80 wt. % mullite and from about 60 to 20 wt. % yttrium silicate.

35. An article according to claim 31 wherein said intermediate layer comprises from about 40 to 80 wt. % mullite and from about 60 to 20 wt. % calcium aluminosilicate.

36. An article according to claim 31 wherein the barrier layer comprises barium.

37. An article according to claim 31 wherein the barrier layer comprises barium oxide.

38. An article according to claim 31 wherein the barrier layer comprises a barium aluminosilicate.

39. An article according to claim 31 wherein the barrier layer comprises a barium strontium aluminosilicate.

40. An article according to claim 31 wherein the barrier layer comprises from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole SrO, about 1.0 mole Al₂O₃ and about 2.00 mole SiO₂, wherein the total of BaO and SrO is about 1.00 mole.

41. An article according to claim 31 wherein the barrier layer consists essentially of from about 0.00 to 1.00 mole BaO, from about 0.00 to 1.00 mole of an oxide of a second alkaline earth metal, about 1.00 mole Al₂O₃ and about 2.00 mole SiO₂, wherein BaO plus the other alkaline earth metal total 1 mole.

42. An article according to claim 31 wherein the barrier layer comprises from about 0.10 mole to about 0.90 mole BaO and from about 0.10 mole to about 0.90 mole SrO.

43. An article according to claim 31 wherein the barrier layer comprises from about 0.25 mole to about 0.75 mole BaO and from about 0.25 mole to about 0.75 mole SrO.

44. An article according to claim 31 wherein the barrier layer comprises about 0.75 mole BaO and about 0.25 mole SrO.

45. An article according to claim 41 wherein the barrier layer comprises from about 0.10 mole to about 0.90 mole BaO and from about 0.10 mole to about 0.90 mole second alkaline earth oxide.

46. An article according to claim 41 wherein the barrier layer comprises from about 0.25 mole to about 0.75 mole BaO and from about 0.25 mole to about 0.75 mole second alkaline earth oxide.

47. An article according to claim 41 wherein the barrier layer comprises about 0.75 mole BaO and about 0.25 mole second alkaline earth oxide.

48. An article according to claim 38 wherein the crystallographic structure of the barrier layer is at least 50% by volume celsian.

49. An article according to claim 39 wherein the crystallographic structure of the barrier layer is at least 50% by volume celsian.

50. An article according to claim 40 wherein the crystallographic structure of the barrier layer is at least 50% by volume celsian.

51. An article according to claim 41 wherein the crystallographic structure of the barrier layer is at least 50% by volume celsian.

52. An article according to claim 42 wherein the crystallographic structure of the barrier layer is at least 50% by volume celsian.

53. An article comprising:

- a substrate comprising silicon; and
- a gaseous species of Si formation inhibiting barrier layer, wherein the barrier layer consists essentially of BaO up to 1.00 mole, from about 0.00 to 1.00 mole of an oxide of a second alkaline earth metal, about 1.00 mole Al₂O₃ and about 2.00 mole SiO₂, wherein BaO plus the other alkaline earth metal oxide total 1 mole inhibits the formation of a gaseous species of Si when the article is exposed to a high temperature, aqueous environment.
UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,410,148 B1
DATED : June 25, 2002
INVENTOR(S) : Harry Edwin Eaton, Jr. et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 8,
Line 3, change the dependency from "12" to -- 1 --.

Column 9,
Lines 36 and 39, change the dependency from "31" to -- 40 --.

Column 10,
Line 1, change the dependency from "31" to -- 40 --.

Signed and Sealed this

Twelfth Day of August, 2003

JAMES E. ROGAN
Director of the United States Patent and Trademark Office