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**Eaton, Jr. et al.**

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(54) **SILICON BASED SUBSTRATE WITH  
CALCIUM ALUMINOSILICATE/THERMAL  
BARRIER LAYER**

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#### Related U.S. Application Data

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1999.  
(51) **Int. Cl.**<sup>7</sup> ..... **B05D 3/00**; C23C 4/10;  
C23C 4/12  
(52) **U.S. Cl.** ..... **427/453**; 427/452; 427/299;  
427/307  
(58) **Field of Search** ..... 427/452, 453,  
427/455, 299, 307

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#### (57) ABSTRACT

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 com-  
prises a calcium alumino silicate.

**20 Claims, 2 Drawing Sheets**

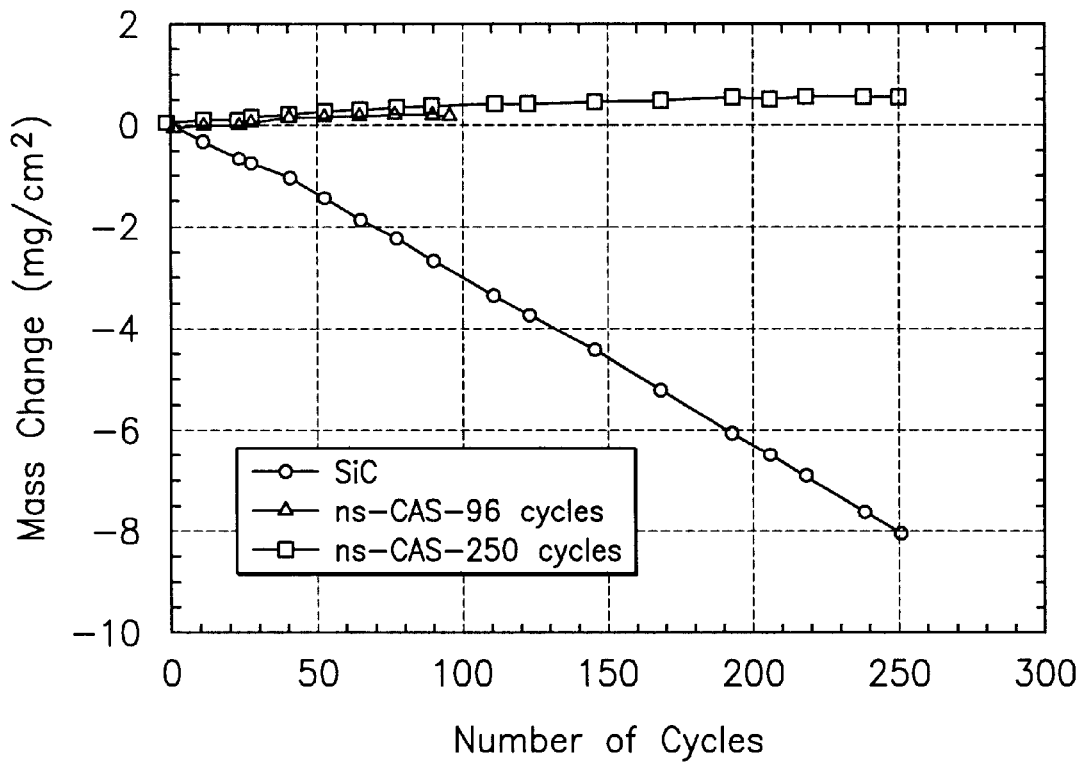
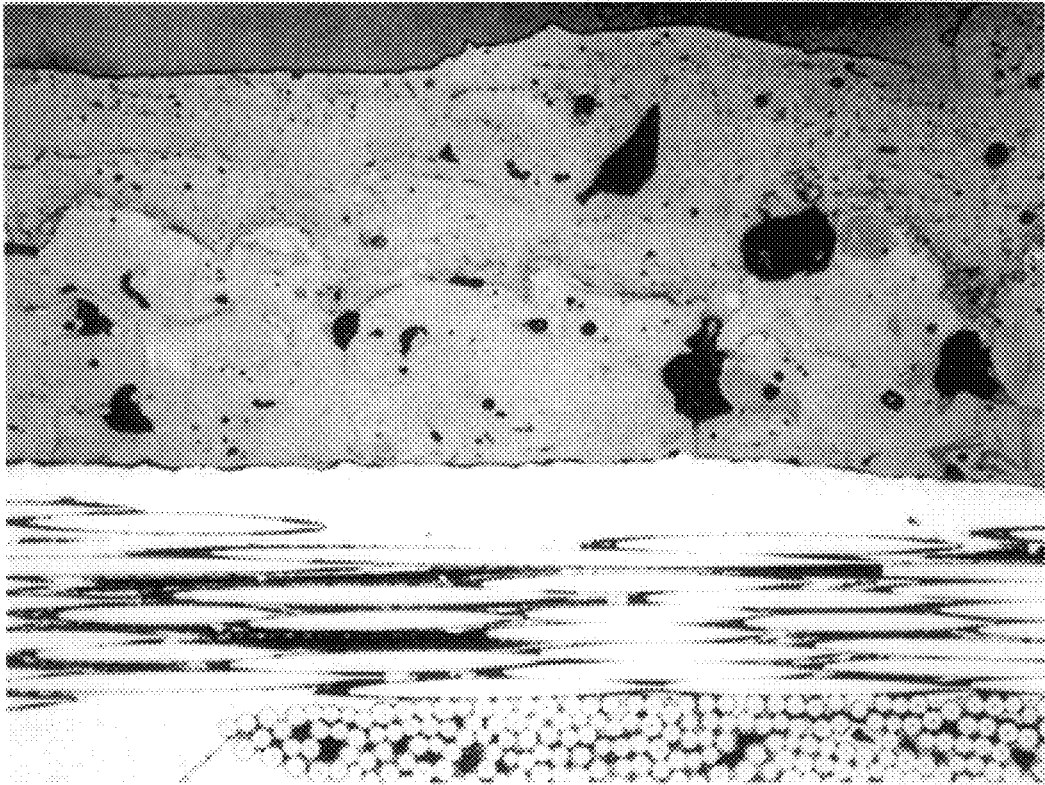


FIG. 1



*FIG. 2*

## SILICON BASED SUBSTRATE WITH CALCIUM ALUMINOSILICATE/THERMAL BARRIER LAYER

This is a Division, of application Ser. No. 09/292,350 filed Apr. 15, 1999.

This invention was made with government support under Contract No. NAS3-26385 awarded by NASA. The government may have certain rights in the invention.

### BACKGROUND OF THE INVENTION

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  $\text{Si}(\text{OH})_x$ , 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  $\text{Si}(\text{OH})_x$  and  $\text{SiO}$  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  $\text{Si}(\text{OH})_x$ . Naturally it would be highly desirable to provide an external barrier coating for silicon containing substrates which would inhibit the formation of volatile silicon species,  $\text{Si}(\text{OH})_x$ , and  $\text{SiO}$ , 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  $\text{Si}(\text{OH})_x$ , 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  $\text{Si}(\text{OH})_x$ , and/or  $\text{SiO}$  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 calcium aluminosilicate barrier layer. 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) serve(s) 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 hereinbelow 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; and

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

### DETAILED DESCRIPTION

The present invention relates to an article comprising a silicon 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 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 materials 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 use as substrates for the article of the present invention include molybdenum-silicon alloys, niobium-silicon alloys and iron-silicon alloys.

Barrier layers particularly useful in the article of the present invention include alkaline earth metal aluminosilicates. In accordance with a preferred embodiment, calcium aluminosilicates are preferred. In a particular embodiment,

the barrier layer comprises greater than about 20% by weight CaO, greater than about 38% by weight  $\text{Al}_2\text{O}_3$  and greater than about 30% by weight  $\text{SiO}_2$ . A particularly suitable barrier layer for use on silicon containing ceramic compositions in the article of the present invention comprises about 24% by weight CaO, about 40% by weight  $\text{Al}_2\text{O}_3$ , and about 36% by weight  $\text{SiO}_2$ . Non-stoichiometric calcium aluminosilicate is preferred.

It is an important feature of the present invention to maintain compatibility between the coefficient of thermal expansion of the silicon containing substrate and the barrier layer. In accordance with the present invention it has been found that the coefficient of thermal expansion of the barrier layer should be within  $\pm 3.0$  ppm per degrees centigrade, preferably  $\pm 0.5$  ppm per degrees centigrade, of the coefficient of thermal expansion of the silicon containing substrate. When using a silicon containing ceramic substrate such as a silicon carbide or a silicon nitride matrix with or without reinforcing fibers as described above in combination with the preferred calcium aluminosilicate barrier layer of the present invention, the desired thermal compatibility with respect to expansion coefficient between the silicon containing substrate and the barrier layer should be  $\pm 2.00$  ppm per degrees centigrade.

The barrier layer should be present in the article at a thickness of greater than or equal to about 0.5 mils (0.0005 inch), preferably between about 3 to about 30 mils and ideally between about 3 to about 5 mils. The barrier layer may be applied to the silicon containing substrate by any suitable manner known in the art, however, it is preferable that the barrier layer be applied by thermal spraying as will be described hereinbelow.

In a further embodiment of the article of the present invention, an intermediate layer can be provided between the silicon containing substrate and the barrier layer. The intermediate layer(s) serve(s) to provide enhanced adhesion between the barrier layer and the substrate and/or to prevent reactions between the barrier layer and the substrate. The intermediate layer consists of, for example,  $\text{SiO}_2$ , mullite, mullite-barium strontium aluminosilicate, mullite-yttrium silicate, mullite-calcium aluminosilicate, and silicon metal. Mullite has been found to be a particularly useful intermediate layer; however, mullite by itself tends to be cracked as the result of thermal spraying fabrication processing. Accordingly, it is preferred that the barrier layer comprises mullite-barium strontium aluminosilicate, mullite-yttrium silicate, or mullite-calcium aluminosilicate in an amount of between about 40 to 80 wt. % mullite and between about 20 to 60 wt. % barium strontium aluminosilicate or yttrium silicate or calcium aluminosilicate. 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 hereinbelow.

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 based substrate may be pre-oxidized to provide a  $\text{SiO}_2$  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 as-sprayed, splat quenched, microstructure and to provide a means to manage stresses which control delamination.

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 substrate, it has been found that the grit blasting should be carried out with  $\text{Al}_2\text{O}_3$  particles, preferably of a particle size of  $\leq 30$  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.  $\text{SiO}_2$  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, and to promote bonding between the sprayed powder particles and between the layers and the substrate. Broadly, the heat treatment step requires a controlled heating of the article over time in a manner which allows for crystallization of the calcium aluminosilicate without swelling and/or formation of pores by the barrier layer. Preferably, the article is heated from room temperature to a temperature of between about 1275° C. to about 1300° C. at a rate of between about 5° C./minute to about 10° C./minute and held at intermediate temperatures wherein the total treatment time is greater than or equal to 68 hours. Specifically, for a barrier layer which comprises non-stoichiometric calcium aluminosilicate, the following heat treatment has been found to be particularly useful for obtaining a non-swelled, substantially porous free barrier layer.

- a) room temperature to 700° C. @ 10° C./min, hold 4 hrs.
- b) 700° C. to 800° C. @ 10° C./min, hold 8 hrs.
- c) 800° C. to 900° C. @ 10° C./min, hold 16 hrs.
- d) 900° C. to 1000° C. @ 10° C./min, hold 16 hrs.
- e) 1000° C. to 1100° C. @ 10° C./min, hold 8 hrs.

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- f) 1100° C. to 1200° C. @ 10° C./min, hold 8 hrs.
- g) 1200° C. to 1225° C. @ 5° C./min, hold 2 hrs.
- h) 1225° C. to 1250° C. @ 5° C./min, hold 2 hrs.
- i) 1250° C. to 1275° C. @ 5° C./min, hold 2 hrs.
- j) 1275° C. to 1300° C. @ 5° C./min, hold 2 hrs.
- k) furnace cool to room temperature.

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

EXAMPLE 1

Hot pressed bulk coupons of non-stoichiometric calcium aluminosilicate (ns-CAS) of composition 24% CaO, 40% Al<sub>2</sub>O<sub>3</sub> and 36% SiO<sub>2</sub> by weight were fabricated via hot pressing in Argon at 1400° C. for 2 hours and then submitted for high steam thermal cycle testing at 1200° C. for up to 250 thermal cycles in comparison to silicon carbide. The results show that the silicon carbide loses up to 8 mg/cm<sup>2</sup> weight during the testing while the ns-CAS does not. See FIG. 1.

EXAMPLE 2

FIG. 2 is a cross section of a 4 mil thick ns-CAS coating on 4 mils of mullite on SiC composite. The ns-CAS and mullite were thermal sprayed onto the silicon carbide composite using the following parameters:

Parameter	Setting
plasma torch	Metco 3M
nozzle	GH
anode	std.
powder port	metco #2
primary gas	Ar @ 80 Metco gage
secondary gas	H2 @ Metco gage
substrate temp.	850 ° C.
carrier gas	Ar @ 37 Metco gage
powder feed	15 to 25 gpm
intermed.	surface
power 30 kw	25 kw
stand-off 2.5-3"	5"

Prior to coating the substrate was cleaned by grit blasting with 27 micron alumina particles at an impact velocity of 150 to 200 mps. The ns-CAS powder was obtained from Specialty Glass as a free flowing -200+400 mesh powder. The mullite was Cerac Mullite (Aluminum Oxide—Silicon Oxide), -150, +325 mesh, Cerac # A-1226. As can be seen from FIG. 2, the invention results in an excellent barrier layer structure.

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. A method for preparing an article comprising the steps of:
  - providing a substrate comprising silicon; and
  - applying a calcium containing gaseous species of Si formation inhibiting barrier layer to the substrate wherein the barrier layer inhibits the formation of gaseous species of Si when the article is exposed to a high temperature, aqueous environment.
2. A method according to claim 1 wherein the coefficient of thermal expansion of the barrier layer is within ±3.0 ppm/° C. the coefficient of thermal expansion of the substrate.

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3. A method 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 substrate.
4. A method according to claim 1 further including the step of grit blasting the substrate prior to applying the barrier layer.
5. A method according to claim 4 including grit blast with alumina particles having a particle size of ≅30 microns.
6. A method according to claim 5 including grit blasting at a velocity of between about 150m/sec to 200m/sec.
7. A method according to claim 1 including applying the barrier layer by thermal spraying.
8. A method according to claim 1 including the step of preoxidizing the substrate to form a layer of SiO<sub>2</sub> prior to applying the barrier layer.
9. A method according to claim 8 wherein the preoxidizing comprises heating the substrate at a temperature of between about 800° C. to 2000° C. for about 15 minutes to 100 hours.
10. A method according to claim 11 including the step of, after applying the barrier layer, heat treating the article.
11. A method according to claim 1 including thermal spraying at a temperature of between about 800° C. to 1200° C.
12. A method according to claim 1 wherein the coefficient of thermal expansion of the barrier layer is within ±3.0 ppm/° C. the coefficient of thermal expansion of the substrate.
13. A method 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 substrate.
14. A method according to claim 1 wherein the barrier layer comprises greater than about 20% by weight CaO, greater than about 38% by weight Al<sub>2</sub>O<sub>3</sub> and greater than about 30% by weight SiO<sub>2</sub>.
15. A method according to claim 1 wherein the barrier layer comprises about 24% by weight CaO, about 40% by weight Al<sub>2</sub>O<sub>3</sub> and about 36% by weight SiO<sub>2</sub>.
16. A method according to claim 1 wherein the barrier layer is non-stoichiometric calcium aluminosilicate.
17. A method according to claim 14 including heat treating said article over time to a temperature which allows for crystallization of the calcium aluminosilicate without swelling and/or the formation of pores by the barrier layer.
18. A method according to claim 17 including heating the article from room temperature to a temperature of between about 1275° C. to about 1300° C. over a time period of at least 68 hours.
19. A method according to claim 18 wherein the article is heated in a stepwise manner at a heat rate of between about 50° C./min to about 3° C./min and held at at least one intermediate temperature.
20. A method according to claim 19 wherein said article is heat treated as follows:
  - a) room temperature to 700° C. @ 10° C./min, hold 4 hrs.;
  - b) 700° C. to 800° C. @ 10° C./min, hold 8 hrs.;
  - c) 800° C. to 900° C. @ 10° C./min, hold 16 hrs.;
  - d) 900° C. to 1000° C. @ 10° C./min, hold 16 hrs.;
  - e) 1000° C. to 1100° C. @ 10° C./min, hold 8 hrs.;
  - f) 1100° C. to 1200° C. @ 10° C./min, hold 8 hrs.;
  - g) 1200° C. to 1225° C. @ 5° C./min, hold 2 hrs.;
  - h) 1225° C. to 1250° C. @ 5° C./min, hold 2 hrs.;
  - i) 1250° C. to 1275° C. @ 5° C./min, hold 2 hrs.;
  - j) 1275° C. to 3000° C. @ 5° C./min, hold 2 hrs.; and
  - k) furnace cool to room temperature.

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,284,325 B1  
DATED : September 4, 2001  
INVENTOR(S) : Harry Edwin Eaton, Jr. et al.

Page 1 of 1

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

Title page.

Item [54], Title, after "ALUMINOSILICATE" and before the "/" insert  
-- ENVIRONMENTAL --.

Column 1.

Line 40, after "Si (OH)<sub>x</sub>" delete the ",".  
Line 63, after "Si (OH)<sub>x</sub>" delete the ",".

Column 6.

Line 18, correct "2000°C" to -- 1200°C --.  
Line 20, correct "11" to read -- 1 --.  
Line 22, correct "1" to read -- 7 --.  
Line 64, correct "3000°C" to read -- 1300°C --.

Signed and Sealed this

Twenty-sixth Day of November, 2002

Attest:



Attesting Officer

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