ABSTRACT

A thermal protection system (TPS) comprising a mixture of silicon carbide and SiOx that has been converted from Si that is present in a collection of diatom frustules and at least one diatom has quasi-periodic pore-to-pore separation distance d(p-p) in a selected range. Where a heat shield comprising the converted SiC/SiOx frustules receives radiation, associated with atmospheric (re)entry, a portion of this radiation is reflected so that radiation loading of the heat shield is reduced.

12 Claims, 7 Drawing Sheets
References Cited

OTHER PUBLICATIONS


* cited by examiner
Cumulative Radiance (CR)
Planck Radiance at T = 9887 deg K (PR)
Atomic Line Radiance at 10 km/sec (ALR)

FIG. 1
FIG. 2
Refractive Index INFO
SiC (Silicon carbide)
Singh et al 1971 - a - SiC: n(\(\phi\)) 0.488-1.064 \(\mu\)m

FIG. 3A
Refractive Index INFO

SiO₂ (Silicon dioxide, Silica, Quartz)

Malitson 1965 - Fused silica: n 0.21-3.71 μm

FIG. 3B
FIG. 4
FIG. 5
Heat Shield

Convec. Heating Mode

Convective

Conducted

Conducted Reradiated

Radiative Heating Mode

SL Radiation Diatoms reflect radiation

Reflected

FIG. 6
I

BIOLOGICALLY INSPIRED RADIATION REFLECTOR

BACKGROUND OF THE INVENTION

There is a clear and continuing need for a thermal protection system (TPS) for a re-entering vehicle (RV) that can withstand heating from a high speed entry or re-entry into an atmosphere of a planetary body that is adaptable enough to accommodate human missions and robotic missions. RV surface heating has two primary sources (1) convective heating (proportional to (velocity)^3) from flow of hot gases past the surface and from chemical combination reactions in the gases; and (2) radiation heating (approximately proportional to (velocity)^6) from a shock wave that forms preceding the RV.

During high speed initial atmospheric entries, as much as 90 percent of the surface heating can arise through radiation from a reacting shock layer. Where a substantial part of this radiation can be reflected from a heat shield, and prevented from contacting or directed away from the RV surface, the overall heat load can be reduced accordingly, which allows reduced heat shield mass and corresponding greater mass for the re-entrant vehicle. Where a TPS can be developed that withstands a large portion of the convective and radiative heating encountered during a high velocity planetary entry, the risk for a crewed mission is reduced, and shorter transit times and higher re-entry velocities, exceeding 15 km/sec (53,651 mi/hour), can be used.

Radiative heating of an RV and its heat shield peaks early in a re-entry interval into an atmosphere, and this heating often arises from specific, limited ranges of wavelengths of concern, (λ,rad), dependent upon atmospheric composition, as indicated in FIG. 1. Provision of a heat shield that has an approximately periodic structure that is preferentially reflective for wavelengths in the range (λ,rad) would reduce the fraction of radiation that contacts the RV surface. However, construction of such a heat shield is likely to be expensive and technically demanding. Preferably, the primary heat shield material is refractory and has a high phase change temperature for ablating.

SUMMARY OF THE INVENTION

These needs are met by the invention, which provides a new heat shield material that: (1) is initially a natural material with a quasi-periodic pore sub-structure; and (2) is processed to form a refractory mixture (e.g., SiC and SiO_x) with superior radiation reflection, phase change and thermal characteristics over the wavelength range (λ,rad). The initial natural material is a collection of diatoms, comprising primarily SiO_x and having pore-to-pore separations d, within an individual diatom, in a selected range D1≤d≤D2 (D1 and/or D2≈100 μm), with particular diatoms preferably chosen for desired diatom pore dimensions. These diatoms react with gaseous Mg at T=600°C to form MgO, which is leached from the diatom structure with an acid to form a pure Si frustule. The frustule is then reacted with H_2 and a hydrocarbon gas, such as CH_4 or C_2H_4 or C_2H_6, to form a mixture of SiO_x and SiC (crystalline and/or amorphous), with the degree of crystallinity being estimatable by X-ray diffraction. MgO is formed in preference to formation of either of the compounds, MgSi and/or MgSiO_x, which would resist removal of the Mg.

A heat shield material additive, comprising a mixture of SiC and SiO_x with a quasi-periodic diatom pore structure and prepared in this manner, may have a high phase change temperature (melting, ablation, evaporation, sublimation, etc.), and has a bulk optical reflectivity OR of at least about 0.19 or 0.033 for normal incidence. Incident radiation may also be photonically reflected at much higher values of OR. Other processing details are discussed in a Description of the Invention. The optical reflectivity value OR tends to increase with increasing incidence angle of radiation received at the heat shield component.

The additive may be a continuous layer. Alternatively, the additive is incorporated onto an exposed surface of the substrate heat shield material by impregnation, coating or similar techniques that may produce non-continuous or isolated deposits the additive. This reflecting additive layer would be operable primarily during an initial time interval (e.g., the first 30-60 sec of re-entry).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 graphically presents an estimate of a radiation spectrum provided by shock layer atomic line radiance (ALR), as a function of wavelength λ for an assumed shock layer temperature T(rad;SL)=10,000°C and a corresponding estimated heat shield temperature T(rad;HS)=4,000°C, in an environment that is initially substantially free of atomic oxygen; FIG. 1 includes, for comparison, a Planck spectrum (PR) of black body radiance and cumulative radiance (CR) for a temperature T=4,000°C (4273°K).

FIG. 2 schematically illustrates an FBR conversion method used here.

FIGS. 3A and 3B graphically present refractive indices n(λ;T) for SiC and for SiO_x, for visible and mid-infrared wavelengths λ.

FIG. 4 indicates graphically a development of temperature adjacent to a temperature at which phase change occurs (melting, ablation, evaporation, sublimation, etc.), according to a conventional view.

FIG. 5 graphically presents an estimation of solution of heat equation for a semi-infinite, one dimensional solid with radiation input at a boundary.

FIG. 6 illustrates reflection/re-radiation that is examined here.

DESCRIPTION OF THE INVENTION

The invention relies for the initial (natural) material upon diatoms containing diatomite (diatomaceous earth), a sedi-
mentary rock composed of fossilized skeletons of diatoms, which are one-celled, algae-like, micron-sized, mostly photosynthetic phytoplankton. Diatomite composition is mainly amorphous SiO₂, with a quasi-periodic arrangement of interconnected pores of nanometer size. These quasi-periodic structures give diatomite some useful photon interaction characteristics.

Each diatom is bounded by a silica frustule or cell wall, including two valves of slightly different size that fit together in a connective zone, known as a girdle, and enclose the remainder of a diatom. An estimated 100,000 species of diatoms are extant in the oceans, usually restricted to the photic zone. Diatom diameters normally range from 40 nm to 200 µm, with pore-to-pore separations that are consistent with a preferred wavelength range \( \lambda_{\text{pred}} \).

The diatoms initially comprise SiO₂. A goal here is to transform the diatoms into a material with a higher phase change temperature, while retaining a quasi-periodic pore structure within a diatom that provides an enhanced photon-reflecting structure.

The transformation or conversion process begins with addition of Mg(gas) to a powder bed of diatom frustules, which comprise SiO₂ (x=1) in a heated Fluid Bed Reactor (FBR) at a temperature T(FBR)=600° C. Mg(solid) is heated in a connective zone, known as a girdle, and enclose the remainder of a diatom. An estimated 100,000 species of diatoms are extant in the oceans, usually restricted to the photic zone. Diatom diameters normally range from 40 nm to 200 µm, with pore-to-pore separations that are consistent with a preferred wavelength range \( \lambda_{\text{pred}} \).

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The transformation or conversion process begins with addition of Mg(gas) to a powder bed of diatom frustules, which comprise SiO₂ (x=1) in a heated Fluid Bed Reactor (FBR) at a temperature T(FBR)=600° C. Mg(solid) is heated and Mg(gas) particles react with SiO₂ to form MgO in a first reaction.

\[
2\text{Mg(gas)}+\text{SiO}_2+\text{Ar} \rightarrow \text{Si(solid)}+2\text{MgO(solid)}+\text{Ar}, \quad (1)
\]

We have found that use of high heating rates in this reaction, together with extended temperature pauses at T=850° C., produce competing magnesium silicides (MgSi) and magnesium silicates (MgSiO₃), which are compounds that will not leach or surrender the Mg (undesirable). Use of moderate temperatures, preferably no higher than T=640-800° C. and for no longer than a selected time interval, At=1 hour, in this reaction, are preferred. Particle size of the Mg reactant is important. Use of smaller diameter Mg particles (diameter≤100 µm) allows use of lower temperature ramp rates and a longer low temperature pause, with T≤600° C., which avoids or minimizes damaging exothermic reactions.

We have also found that Mg particles react with the crystalline SiO₂ quartz walls of the FBR and undergo the same conversion process as amorphous SiO₂ frustules, but with reaction rates much lower than the SO₂ frustules. This lower reaction rate damages the FBR.

In a second reaction, MgO is leached from the diatom structure with HCl or another modest strength acid to provide frustule structures containing primarily Si,

\[
\text{Si}+\text{MgO}+2\text{HCl}+\text{Ar} \rightarrow \text{SiCl}_4+\text{MgCl}_2+2\text{H}_2+\text{Ar}, \quad (2)
\]

In a third reaction, the Si frustule is reacted with a hydrocarbon gas (CH₄, C₂H₆, C₂H₄, etc.) and with H₂ gas in the FBR to form an SiC frustule,

\[
\text{SiC}_2+\text{H}_2+\text{Ar} \rightarrow \text{SiC}+\text{H}_2+\text{Ar}, \quad (3-1)
\]

\[
2\text{SiC}_2+\text{H}_2+\text{Ar} \rightarrow 2\text{SiC}+2\text{H}_2+\text{Ar}, \quad (3-2)
\]

\[
2\text{SiC}_2+\text{H}_2+\text{Ar} \rightarrow 2\text{SiC}+4\text{H}_2+\text{Ar}, \quad (3-3)
\]

An assembly of SiC frustules, formed at temperatures (T1\(=800° \text{C.}\), preferably T2\(=650° \text{C.}\), will likely be amorphous. SiC frustules formed in the third reaction (3-1,2,3) will require higher temperatures to increase crystallinity fraction. Conversion to SiC frustules may be faster and use lower temperatures than normal. Conversion of the SiO₂ to SiC by this process may not be complete so that the substances produced by this process may be a mixture comprising SiC and SiO₂.

A first estimate of optical reflectivity \( R(\lambda; T) \) associated with the first sublayer Subl, assumes that all sublimated SiC material is promptly removed from a region adjacent to Subl. and that the local environment comprises a heated first sublayer material with an associated refractive index \( n(\lambda; T) \) and a contiguous second layer that is substantially a vacuum, with associated refractive index \( n=1 \), as illustrated in FIG. 3A. Assuming that the first layer/second layer interface IF is not too rough, an abrupt change in refractive index at this interface will have an associated optical reflectivity at normal incidence of

\[
R(\lambda; T)=[(n(\lambda; T)-1)/(n(\lambda; T)+1)]^2, \quad (4)
\]

which has a value of about 0.204 for room temperature SiC and for a wavelength \( \lambda=589 \text{ nm} \). This ignores a small difference between ordinary and extraordinary refractive indices, \( n_o=2.484 \) and \( n_e=2.691 \), of SiC at these conditions.
Estimates of variation of refractive index n(λ;T) with wavelength λ for bulk SiC, illustrated in FIG. 3A, indicate that the index decreases from about n(λ;T)=2.09 at λ=500 nm toward n(λ;T)=2.55 as wavelength λ increases toward and beyond 3000 nm. From examination of FIG. 1, it appears that (1) peak shock layer radiation intensity occurs at a wavelength λ(peak)≈680 nm, which is consistent with a peak wavelength value, λ(Planck;peak)≈676 nm for a Planck black body radiation curve, using the Wien displacement law,
\[
λ(\text{nm} k(°K)^{-1}) = 0.00289,
\]
with an assumed temperature of T=4273° K. The wavelength range [λ<0.011 to >0.007] of interest in this situation is approximately 190 nm (vacuum uv) to 3000 nm so that use of a refractive index, n(λ;T)≥2.55, with associated bulk SiC optical reflectivity, OR(λ;T;SiC)=0.19, appears to be reason-able for modest temperatures.

FIG. 3B graphically illustrates variation of refractive index n(λ;T;SiO x) with wavelength for a wavelength range of interest here. Where SiO x is the bulk material, assuming that the first/second block interface II is not too rough, an abrupt change in refractive index of SiO x at this interface (n(λ;T)=1→n(λ;T)=1.45 at λ=589 nm) will have an associated optical reflectivity at normal incidence, according to Eq. (4), of OR(λ;T;SiO x)=0.034. The refractive index n(λ;T;SiO x) and the optical reflectivity OR(λ;T;SiO x) will decrease further as wavelength increases toward and beyond λ=3000 nm.

Example: Some Optimal Choices of Diatom Parameters.

The optical reflectivity OR(λ;T) of a block of material (not removed) may be enhanced by choosing a diatom species with nearest neighbor pore separation distances d(p-p) (measured laterally) having selected values that are approximately equal to optimal values estimated in the technical literature. For example, in N. Komarevskiy et al, “Potential of glassy carbon and silicon carbide photonic structures as electromagnetic radiation shields for atmospheric re-entry” Optics Express, Vol 20, No 13 (11 Jun. 2012), Sec. 6, Table 2, the authors analyze a “porous reflector” model for SiC. The authors find several pore-to-pore separation distances for optimal reflection of radiation in a wavelength range λ≈7200-1400 nm, which lie in a selected range, d(p-p)=226, 229, 230 and 239 nm (each no more than 300-400 nm), will change according to the physical and geometric situation. Within an individual diatom, the pore-to-pore separation distances d(p-p) will not be precisely the same so that the arrangement of pores will be quasi-periodic rather than strictly periodic. However, from the variety of diatoms available, it is possible to identify and use one or more species with approximately the same (optimal) pore-to-pore separation distances d(p-p).

First Model: SiC/SiO x Layer Located at Exposed Surface of Heat Shield.

In a first model, the transformed diatom material (SiC or SiO x) is provided as a coating or first sub-layer SubL, located at an exposed surface of the heat shield, and experiences an estimated maximum temperature, from shock layer radiation and convective heating, T(rad;max)=4000° C. This maximum HS surface temperature subsequently decreases to lower temperatures over the next 30-60 sec. A first portion of the first sub-layer undergoes phase change in this environment and is treated here as providing no substantial contribution to reflection of radiation received from the shock layer SL. A second (remaining) portion of the first sub-layer is assumed to be intact and to have sufficient (remaining) longitudinal thickness Δl to provide an associated optical reflectivity, OR(λ;T;SiO x)≈0.033, for this second (remaining) portion of the first sub-layer SubL. A lower bound on an initial longitudinal thickness Δl(min) of the first sub-layer SubL can be estimated by the following considerations. Assume that the shock layer radiation power density P(t=δE/dt(mJoules/cm²·sec)) is approximately constant or decreasing with time, where δE(t) is cumulative energy deposited. This power density is anticipated to decrease overall with passage of time, after an initial (re)entry time interval, because the velocity of the (re)entry vehicle RV will decrease as the RV moves through the atmosphere.

Phase change of a volume ΔV of SiC or SiO x requires provision of at least the following radiant energy: (i) a first energy density component ΔE1 that is required to raise the volume ΔV from a reference temperature value T(ref) to a phase change initiation temperature T(ϕ), and (ii) a second measure of energy input ΔE2 required to convert the volume ΔV of initially solid SiC or SiO x material at temperature T(ϕ) to material that has undergone a phase change. With reference to FIG. 4, below and near a phase change temperature T(ϕ), the temperature of a material increases to T(ϕ), then appears to plateau at T=T(ϕ) after the volume ΔV has reached the first energy content ΔE1. The apparent temperature remains at a value T(ϕ) while the volume ΔV accumulates an additional energy increment ΔE2 required for completion of phase change, after which time the temperature may continue to increase, as indicated in FIG. 4 according to a conventional view. This perspective applies for phase change of a volume of SiC or of SiO x.

In a first approximation, it is assumed that each of the energy inputs, ΔE1 and ΔE2, is distributed according to a one-dimensional heat equation for energy distribution, ut(x, t)=temperature in a semi-infinite solid with thermal conductivity k, specific heat capacity c, density ρ, which are temperature-independent, through a solid with cross-sectional area A oriented perpendicular to a direction of transport of temperature.

\[
\frac{\partial u}{\partial t} + \frac{\partial f}{\partial x} = 0, x_0 
\]

\[
\frac{\partial u}{\partial t} + \frac{\partial f}{\partial x} = 0, x_0 
\]
Here, the solid is initially at temperature \( u = 0 \) and is heated by radiation from a source at temperature \( u_0 \). One solution for this formulation is set forth by H.S. Carslaw and J.C. Jaeger in *Conduction of Heat in Solids*, Oxford Press, 1946, pp. 70-73:

\[
\begin{align*}
\phi(x,t) &= a_0 e^{-x/(2\nu t)} - \exp(-x^2/4\nu t) - \text{erf}c\left(x/(2\nu t)\right), \\
\text{erfc}(x) &= 1 - \frac{1}{\sqrt{\pi}} \int_{x}^{\infty} e^{-t^2} \, dt.
\end{align*}
\]

Adjacent to the boundary, \( x = 0 \), the radiation energy deposit in a volume \( \Delta V \) corresponds to Eq. (9), and the heat energy continues to rise at and near this boundary as long as heat transfer across this boundary continues. FIG. 5, adapted from FIG. 9, page 72 of Carslaw and Jaeger, ibid, graphically presents a sequence of curves providing estimates of temperature \( u(x,t)/u_0 \) corresponding to constant values of a dimensionless coordinate,

\[
s = \frac{x}{\sqrt{4\nu t}}(s = 0, 0.1, 0.2, \ldots, 1.5)
\]

When the local heat energy \( (pc)u(x,t) \) reaches a value \( \Delta E1 \), the temperature in a local volume \( \Delta V \) has reached a first value at which the phase change process begins. However, the local heat energy \( (pc)u(x,t) \) must reach an energy value, \( \Delta E1 + \Delta E2 \), in order to complete the phase change process in the local volume \( \Delta V \). This analysis will focus primarily on the total energy, \( \Delta E1 + \Delta E2 \), required to complete the phase change process in the local volume \( \Delta V \).

Phase change is initiated for a portion of the solid, given by the condition

\[
(s(x(t,\Delta E1); A)) = \text{erf}(x/(\sqrt{4\nu t})),
\]

for which the corresponding heat energy satisfies

\[
(pc)u(x(t,\Delta E1); A) = \Delta E1.
\]

Phased change, once begun, is completed for a portion of the solid defined by condition

\[
(s(x(t,\Delta E2); A)) = \text{erf}(x/(\sqrt{4\nu t})) + \text{erf}(x/(\sqrt{4\nu t})),
\]

for which the corresponding heat energy satisfies

\[
(pc)u(x(t,\Delta E2); A) = \Delta E1 + \Delta E2.
\]

The model of phase change represented in FIG. 4 is implemented as follows. For a fixed coordinate value \( x(0) \) and variable time value \( t \), a measure of heat energy, \( (pc)u(x(t)) \), satisfies \( (pc)u(x(t)) = \Delta E1 + \Delta E2 \) until time \( t \) reaches a threshold time value,

\[
t(\Delta E1 + \Delta E2),
\]

where the threshold time value \( t(\Delta E1 + \Delta E2) \) corresponds to completion of phase change at that value of the coordinate \( x \), and \( t(\Delta E1 + \Delta E2) \) increases monotonically with increasing \( x \).

In FIG. 5, a horizontal line \( H-H \), corresponding to an arbitrary fraction \( \psi = u/u_0 = 0.7 \) of the maximum heat energy value, \( (pc)u(x = 0, t) \), present in a volume \( \Delta V \), is shown for the normalized temperature \( u/u_0 \). The line \( H-H \) indicates that, for values of the dimensionless coordinate \( s = x/(\sqrt{4\nu t}) \) greater than \( s(\text{max}) = 0.27 \), a volume \( \Delta V \) located at the corresponding coordinate pair \( (x, t) \) cannot attain or exceed the corresponding normalized temperature, \( \psi = u/u_0 = 0.7 \). Where the fraction \( \psi = 0.7 \) is interpreted as corresponding to achievement of complete phase change, a volume \( \Delta V \), located at a coordinate \( x \) corresponding to \( s = 0.27 \), cannot (yet) complete the phase change. The numerical value of the fraction \( \psi \) of maximum heat energy actually chosen will depend upon the power density value provided by the shock layer radiation and upon the total energy, \( \Delta E1 + \Delta E2 \), required for completion of phase change for the volume \( \Delta V \). The portion of the solid for which the phase change process is completed may pass away as a gas or vapor so that an initial thickness value \( \tau \) of the SiC or SiO\(_x\) material will decrease as time increases.

Assume that an initial thickness, defined by \( 0s(x; \Delta E1 + \Delta E2) \) is assumed to correspond to a fraction \( \psi_0 \) for the dimensionless quantity \( u/u_0 \) in the sequence of curves presented in FIG. 5. A horizontal line, \( \psi = \psi_0 \) is drawn in FIG. 5, and a survival value,

\[
s(\text{surv}) = x/(\sqrt{4\nu t}(\text{surv}))
\]

of the dimensionless variable \( s \) is computed and compared with the horizontal line \( \psi = \psi_0 \) in FIG. 5. Where the value \( s(\text{surv}) \) lies above the horizontal line, \( \psi = \psi_0 \), in a graph corresponding to FIG. 5, a portion of the initial thickness, \( 0s(x; \Delta E1 + \Delta E2) \), of the SiC or SiO\(_x\) material will survive the phase change process for (at least) a survival time interval length \( \Delta(t(\text{surv})) \). The portion of the thickness \( x \) that does not survive the phase change process serves as a sacrificial layer. The fractional value, \( \psi = \psi_0 \), used here may be used as a zeroth order estimate of optical reflectivity OR for this model.

Where the survival value \( s(\text{surv}) \) lies on or below the horizontal line, \( \psi = \psi_0 \), in a graph corresponding to FIG. 5, no portion of the initial thickness, \( 0s(x; \Delta E1 + \Delta E2) \), of the SiC or SiO\(_x\) material will survive. When the SiC or SiO\(_x\) material thickness has decreased below a minimum thickness \( \tau(\lambda_{\text{rad}}) \), dependent upon a representative wavelength \( \lambda_{\text{rad}} \) of the incident radiation, optical reflectivity OR from this remaining layer will likely decrease toward 0.

Second Model: SiC/SiO\(_x\) Material Deposited in Isolated Clusters at Exposed Surface of Heat Shield.

In a second model, the SiC and/or SiO\(_x\) material is deposited in isolated clusters at an exposed surface of another heat shield component on an RV, through impregnation or other deposit process. Each cluster of the SiC and/or SiO\(_x\) deposits has a numerical differential area \( A_j \) (j = 1, . . . , J), which is assumed to be at least equal to a threshold value \( \Delta A(\text{thr}) \) required for reflection. The sum

\[
\Delta A = \sum_{j=1}^{J} A_j
\]

is a fraction \( f(0 < f < 1) \) of the total projected area \( A \) of the exposed surface.

A diatom within each of these deposits of transformed diatom material may be treated as comprising a quasi-periodic array of pores that approximately supports reflection of the incident radiation, with an associated optical reflectivity OR\((j)\) that lies between a lower bound, OR\(\text{bulk; SiC}) = 0.19 \) or OR\(\text{bulk; SiO}_x) = 0.033 \), and a much higher upper bound, OR\(\text{photonic}) \), that would be provided by photonic interaction of the incident radiation with a quasi-periodic pore structure. An estimate of overall optical reflectivity for the exposed surface (area \( A \)) of the heat shield then becomes
for phase change of the material and enhancing refractory
range 2-2,000 µm; some species can be seen with an unaided
remainder of a diatom. Diameters of the diatoms lie in a
connective zone, known as a girdle, and enclose the
in an associated wavelength range and re-radiation of wave-
including two valves of slightly different size that fit together
lengths in another (convective heating) range are separately
illustrated in FIG. 6.

initially a naturally occurring material with a quasi-periodic
thermal protection characteristics in at least one of two
ways: (1) increasing temperatures or heat content required
for phase change of the material and enhancing refractory
behavior of the material; and (2) enhancing photonic behav-
ior and reflection of radiation received by the shield from a
shock layer that forms as the RV enters or re-enters the
atmosphere of a planetary body. The pore structure within a
diatom is quasi-periodic, and an average nearest neighbor
pore-to-pore separation distance (p-p) is preferably chosen
to be approximately equal to one or more of the estimated
optimal periodicity dimensions. The heat content received
by the heat shield and its additive comprises radiation from
a shock layer that forms upon RV entry or re-entry and
convective heating produced by motion of the RV.
The additive provides (i) enhanced reflection of the radia-
tion of wavelengths in a range that corresponds to wave-
lengths of the incident radiation and (ii) re-radiation of the
convective heating received, at wavelengths that are gener-
ally larger than the range of wavelengths that are associated
with convective heating. A primary goal is to reduce sub-
stantially the convective and radiation heat content that is
absorbed by the heat shield and additive. The diatom materi-
al that is processed to provide the additive is initially a naturally occurring material with a quasi-periodic
pore structure within each diatom. The reflection of radiation
in an associated wavelength range and re-radiation of wave-
lengths in another (convective heating) range are separately
illustrated in FIG. 6.


Diatoms are unicellular, eukaryotic, mostly photosyn-
thetic microorganisms that possess exoskeletons (frustules)
comprising amorphous silica (SiOx). Each diatom is
bounded by a frustule or cell wall of silica (hydrated SiOx),
including two valves of slightly different size that fit together
in a connective zone, known as a girdle, and enclose the
remainder of a diatom. Diameters of the diatoms lie in a
range 2-2,000 µm; some species can be seen with an unaided
eye. An estimated 100,000 species of diatoms are extant in
the oceans, usually restricted to the photic zone (extending
to a depth of about 200 feet). Diatom reproduction is
primarily asexual, by binary fission. A typical diatom may
have about 11,000 genes. During “bloom and bust” periods,
diatoms represent as much as 70 percent of the phytoplank-
ton community and produce about 25 percent of the oxygen
on the Earth. A bloom cycle will often terminate because of
depletion of available silicon.

Silicon and magnesium compete for oxygen, but Mg
appears to be attracted more strongly to oxygen than Si is
attracted to oxygen. In one experiment, reported circa 2002,
researchers converted all silica in a diatom into magnesium
oxide MgO. In another experiment, reported in 2004, a
diatom was exposed to titanium dioxide TiO2, which
completely replaced the silica in the diatom.

Diatoms are traditionally divided into two orders: Cent-
trates or centric diatoms have pores or apertures that are
distributed approximately radially symmetric; and Pennate
diatoms have pores or apertures that are distributed approxi-
ately bilaterally symmetric. Diatoms of the same species
consistently form shells or frustules with the same pattern,
which may indicate that the designs are genetically pro-
grammed. Frustules of a diatom will usually have pores or
apertures, often with pore diameter values (pore) of about
40 nm, but with nearest neighbor pore separation distances
(p-p) that have a larger range. The limited range of pore
diameters (pore) allows diatom frustules to be used for
particle sorting and separation.

Centers of diatom pores appear to be distributed in an
approximately hexagonal pattern. Assuming that a regular
hexagon pattern is precisely repeated, with a uniform center-
to-center separation distance (p-p) = 2d1, each hexagon is
the sum of 12 30-60-90 triangles with hypotenuse length (2
d1)/v3 and has an area

\[ A_{(hex)} = (6 \cdot d1^2\cdot v3) \]

(A-1)

Where a single pore of radius \( d_2 \) is located within this
hexagon, the porosity fraction associated with this pattern
has a value

\[ \text{porosity} = \frac{\text{area of } \pi d_2^2 - \pi d_1^2}{\pi d_2^2} \]

(A-2)

A hydrofluoric acid (HF) solution can be used to increase the
pore diameters (pore) for a given diatom. It is unclear what
effect, if any, an HF treatment has on the pore-to-pore
separation distance (p-p).

D. Losic et al, in “Pore Architecture of Diatom Frustules”
1-8, have measured frustule dimensions statistically for two
species, Coscinodiscus sp. and Thalassiosira eccentrica. For the
Coscinodiscus sp., average pore diameter, average pore-
to-pore distance and average porosity value were

\[ d_{(pore)} = 45 \pm 19 \text{ nm} \]
\[ \text{porosity} = 7.5 \pm 1.2\% \]
\[ d_{(p-p)} = 310 \pm 10 \text{ nm (estimate).} \]

Three porous layers of silica are present, and the pore
distribution is approximately radially symmetric for Cosci-
 nodiscus sp. For the T. eccentrica diatom, the corresponding
dimensions were

\[ d_{(pore)} = 40 \pm 6 \text{ nm} \]
\[ \text{porosity} = 10 \pm 2.5\% \]
\[ d_{(p-p)} = 240 \pm 10 \text{ nm (estimate).} \]

For T. eccentric, two porous layers of silica are present,
and the pore distribution is approximately linear (row upon
row, referred to as “concentric”), rather than radially sym-
metric. Pore-to-pore separation distances within an indi-
vidual diatom can be as large as about 2 µm.

What is claimed is:

1. A method for providing a thermal protection compo-
nent for a space vehicle that enters or re-enters an
atmosphere, the method comprising:

(a) providing a plurality of particles, comprising Mg, and
a powder bed of frustules of SiOx (x=1) from diatom
shells in a heated fluidized bed reactor (FBR), where at
least one diatom shell has average nearest neighbor
pore-to-pore spacing \(d(p-p)\) that lies in a selected range,
\(D_1 < d(p-p) < D_2\), with \(D_1 = 100\) nm and \(D_2 = 400\) nm;
(2) heating the plurality of particles and the SiO\(_2\) powder
bed to a first temperature no greater than about 800° C.,
and allowing at least a portion of the particles and the
SiO\(_2\) powder bed to react to form MgO and Si;
(3) leaching MgO to provide a first mixture comprising Si
particles and SiO\(_2\) particles;
(4) providing a hydrocarbon gas, comprising at least one
of \(CH_4\), \(C_2H_4\) and \(C_2H_6\), plus an \(H_2\) gas in the FBR in
a temperature range \(T_2 = 640-800° C\);
(5) allowing the first mixture comprising Si particles and
SiO\(_2\) particles to react with the hydrocarbon gas and
with the \(H_2\) gas in the FBR to form a substance
comprising SiC and SiO\(_2\), wherein at least a portion of
the first mixture is converted to a second mixture
comprising SiC particles and SiO\(_2\) particles, wherein
a temperature during the reaction of the first mixture
with the hydrocarbon gas and with the \(H_2\) gas in the FBR is
no higher than 800° C.;
(6) providing a layer of the second mixture, having an
initial thickness \(t\) at least equal to a selected threshold
temperature \(t(\text{thr})\), on an exposed surface of a heat shield
system;
(7) permitting the layer of the second mixture to receive
radiation from a source of radiation; and
(8) permitting the layer of the second mixture to serve as
an optical reflector to reflect a portion of the radiation
received.

2. The method of claim 1, further comprising choosing
said pore-to-pore spacing \(D_1 = 200\) nm.
3. The method of claim 1, further comprising choosing
said pore-to-pore spacing \(D_2 = 300\) nm.
4. The method of claim 1, wherein said hydrocarbon gas
contains \(C_2H_6\), \(C_2H_4\), or a combination thereof.
5. The method of claim 1, further comprising limiting said
first temperature to a range, \(T_1 = 600-640° C\).
6. The method of claim 1, further comprising choosing
said threshold thickness \(t(\text{thr})\) that is sufficient so that, after
exposure of said second mixture to said radiation for a
selected time interval length \(\Delta t\), a portion of said second
mixture remains on said exposed surface.

7. A method for providing a thermal protection
component for a space vehicle that enters or re-enters an atmo-
sphere, the method comprising:

1. providing a plurality of particles, comprising Mg, and
a powder bed of frustules of SiO\(_2\) (x=1) from diatom
shells in a heated fluidized bed reactor (FBR), where at
least one diatom shell has average nearest neighbor
pore-to-pore spacing \(d(p-p)\) that lies in a selected range,
\(D_1 < d(p-p) < D_2\), with \(D_1 = 100\) nm and \(D_2 = 400\) nm;
(2) heating the plurality of particles and the SiO\(_2\) powder
bed to a first temperature no greater than about 800° C.,
and allowing at least a portion of the particles and the
SiO\(_2\) powder bed to react to form MgO and Si;
(3) leaching MgO to provide a first mixture comprising Si
particles and SiO\(_2\) particles;
(4) providing a hydrocarbon gas, comprising at least one
of \(CH_4\), \(C_2H_4\) and \(C_2H_6\), plus an \(H_2\) gas in the FBR in
a temperature range \(T_2 = 640-800° C\);
(5) allowing the first mixture comprising Si particles and
SiO\(_2\) particles to react with the hydrocarbon gas and
with the \(H_2\) gas in the FBR to form a substance
comprising SiC and SiO\(_2\), whereby at least a portion of
the first mixture is converted to a second mixture
comprising SiC particles and SiO\(_2\) particles, wherein a
temperature during the reaction of the first mixture
with the hydrocarbon gas and with the \(H_2\) gas in the FBR is
no higher than 800° C.;
(6) depositing the second mixture in a plurality of isolated
clusters, at least one cluster having an initial thickness
\(t(\text{thr})\) at least equal to a selected threshold thickness
\(t(\text{thr})\), on an exposed surface of a heat shield system;
(7) permitting the deposit of the second mixture to receive
radiation from a source of radiation; and
(8) permitting the deposit of the second mixture to serve
as an optical reflector to reflect a portion of the radiation
received.

8. The method of claim 7, further comprising choosing
said pore-to-pore spacing \(D_1 = 200\) nm.
9. The method of claim 7, further comprising choosing
said pore-to-pore spacing \(D_2 = 300\) nm.
10. The method of claim 7, wherein said hydrocarbon gas
contains \(C_2H_6\), \(C_2H_4\), or a combination thereof.
11. The method of claim 7, further comprising limiting said
first temperature to a range, \(T_1 = 600-640° C\).
12. The method of claim 7, further comprising choosing
said threshold thickness \(t(\text{thr})\) that is sufficient so that, after
exposure of said second mixture to said radiation for a
selected time interval length \(\Delta t\), a portion of said second
mixture remains on said exposed surface.

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