LIGHT-WEIGHT CERAMIC INSULATION

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Ultra-high temperature, light-weight, ceramic insulation such as ceramic tile is obtained by pyrolyzing a siloxane gel derived from the reaction of at least one organo dialkoxy silane and at least one tetralkoxy silane in an acid or base liquid medium. The reaction mixture of the tetra- and dialkoxy silanes may contain also an effective amount of a mono- or trialkoxy silane to obtain the siloxane gel. The siloxane gel is dried at ambient pressures to form a siloxane ceramic precursor without significant shrinkage. The siloxane ceramic precursor is subsequently pyrolyzed, in an inert atmosphere, to form the black ceramic insulation comprising atoms of silicon, carbon and oxygen. The ceramic insulation, can be characterized as a porous, uniform ceramic tile resistant to oxidation at temperatures ranging as high as 1700° C. and is particularly useful as lightweight tiles for space craft and other high-temperature insulation applications.

19 Claims, No Drawings
LIGHT-WEIGHT CERAMIC INSULATION

ORIGIN OF INVENTION

The invention described herein was made in the performance of work under a NASA Contracts NAS2-97028 and NAS2-98067 and is subject to Public Law 96-517 (35 U.S.C. §200 et seq.). The contractor has elected to retain title in the invention.

BACKGROUND OF INVENTION

1. Field of the Invention

This invention relates to an ultra high-temperature, light-weight ceramic insulation such as porous ceramic tile containing silicon, carbon and oxygen. More particularly, the invention relates to a lightweight, ceramic insulation containing silicon, carbon and oxygen capable of retaining its shape, strength and physical properties when exposed to an oxidizing environment at temperatures as high as 1700°C. More specifically, this invention relates to the sol-gel process of preparing ceramic insulation which comprises an insulation product derived from the reaction of multifunctional silanes to form a small-pore, wet siloxane gel followed by drying the gel at ambient pressures with limited shrinkage and, subsequently heating or pyrolyzing the dried gel, in an inert atmosphere, to form the high-temperature, lightweight ceramic insulation.

An important use for the insulation of this invention includes, for example, the space vehicles, such as the space shuttle which leaves and reenters the earth’s atmosphere and therefore requires exterior thermal insulation. The operation of the space shuttle requires the development of lightweight and thermally efficient exterior insulation capable of withstanding a variety of environments. During reentry into the earth’s atmosphere, the insulation must maintain the vehicle’s exterior structure below 175°C, while experiencing substantial aerodynamic environments which heat the surface of the insulation to temperatures in excess of 1,000°C. In space, the thermal protection must insulate the vehicle from the cold (e.g., -70°C) experienced while in orbit. In addition to thermal and aerodynamic environments, the insulation must be able to withstand the mechanical stress associated with launch vibrations, acoustics, structural movement of the surface of the vehicle, and the landing impact.

The use of state-of-the-art thermal insulation, lightweight ceramic tiles, developed by Lockheed (LI-900), and NASA/Ames Research Center (AETB, AIM, FRCI, etc.), are all limited to temperatures of use at about 1300°C in an oxidizing environment. For applications which experience temperatures above 1300°C, a dense ceramic insulation must be used which adds a substantial weight penalty. Presently, the thermal insulation used for protecting space vehicles includes both the rigid and flexible ceramic insulation, limited to temperatures of use at about 1300°C in an oxidizing environment. For applications which experience temperatures above 1300°C, a dense ceramic insulation must be used which adds a substantial weight penalty. Presently, the thermal insulation used for protecting space vehicles includes both the rigid and flexible ceramic insulation, limited to temperatures of use at about 1300°C in an oxidizing environment. For applications which experience temperatures above 1300°C, a dense ceramic insulation must be used which adds a substantial weight penalty. Presently, the thermal insulation used for protecting space vehicles includes both the rigid and flexible ceramic insulation, limited to temperatures of use at about 1300°C in an oxidizing environment.
alcohol to remove water. The alcogel is thereafter treated in an autoclave by means of a temperature increase to above the critical point of the alcohol, isothermic pressure drop by means of the release of alcohol vapor, and then a temperature drop. U.S. Pat. No. 4,610,863 describes an improved supercritical drying process for forming silical aerogel. The improvement includes the additional step, after alcogels are formed, of substituting a solvent, such as CO₂, for the alcohol in the alcogels, the solvent having a critical temperature less than the critical temperature of the alcohol. The resulting gels are dried at a supercritical temperature for the selected solvent, such as CO₂.

**SUMMARY OF THE INVENTION**

In comparison to the teaching's of the prior art, this invention relates to lightweight, high-temperature ceramic insulation comprising atoms of silicon, carbon and oxygen derived from the reaction of at least one organodialkoxy silane and at least one tetraalkoxy silane to form a siloxane gel in the presence of a catalyst in a liquid medium such as alcohol. In addition, the reaction mixture can include effective amounts of at least one alkyl trialkoxy silane and at least one dialkoxy silane to form wet alcogels, in the presence of a catalyst in a liquid medium followed by drying the alcogel at ambient pressures and subsequently heating or pyrolyzing the dried gel, in an inert atmosphere, to temperatures ranging from about 900°C to 1500°C, to form the ceramic insulation.

The preferred di- and tetra-functional alkoxides are the silicon alkoxides having di- and tetra-oxygen functionality wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively. The silanes particularly useful in the practice of this invention include a combination of silanes wherein the silicon alkoxides have two and four Si—O bonds, respectively.

The reaction ratio of the tetraalkoxy silane to the dialkoxy silane may also contain at least one alkyl monoalkoxy silane having the formula:

\[ R^1 \text{Si}(OR^6)_3 \]

wherein R¹ is a saturated or unsaturated organic radical having 1 to 12 carbons with (b) effective amounts of at least one dialkoxy silane having the formula:

\[ (RO)_{2-n}Si—R'R^n_2 \]

wherein R² is a saturated or unsaturated organic radical having 1 to 12 carbons and R³ and R⁴ are saturated or unsaturated organic radicals having 1 to 12 carbons and R⁵ is either the same or different alkyl radicals.

The reaction of at least one organodialkoxy silane and at least one tetraalkoxy silane to form a siloxane gel in the presence of a catalyst in a liquid medium such as alcohol. In addition, the reaction mixture can include effective amounts of at least one alkyl trialkoxy silane and at least one dialkoxy silane to form wet alcogels, in the presence of a catalyst in a liquid medium followed by drying the alcogel at ambient pressures and subsequently heating or pyrolyzing the dried gel, in an inert atmosphere, to temperatures ranging from about 900°C to 1500°C, to form the ceramic insulation.

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of 1 to 12 carbons. Where the R² and R³ alkyl radicals of the dialkoxy silane have 1–4 carbons, the ratio in the reaction mixture is about 1.0 part by weight of the tetraalkoxy silane to about 0.1 to 2.0 parts by weight of the dialkoxy silane. Where the R² and R³ are alkyl radicals of 1–4 carbons, the ratio in the reaction mixture is about 1.0 part by weight of the tetraalkoxy silane to about 0.1 to 2.0 parts by weight of the dialkoxy silane.

The oxidation-stable, high temperature, porous ceramic insulation materials of this invention can be characterized as being derived from pyrolyzed siloxane gels consisting essentially of silicon, carbon, and oxygen in the molar ratios of about 1.0 mole of silicon, to about 0.1 to 1.0 mole of carbon to about 0.8–2.0 moles of oxygen. This ceramic insulation is further characterized as having black particle sizes ranging from about 1.0 to 50 μm, void sizes ranging from about 10 to 100 μm. It is capable of retaining its insulation and other physical properties at temperatures ranging up to about 1700°C.

Accordingly, it is an object of this invention to provide high temperature, lightweight ceramic insulation for use at temperatures as high as 1700°C.

It is another object of this invention to provide a method of preparing high temperature, lightweight ceramic insulation derived from the reaction of alkoxysilanes containing silicon, oxygen and carbon for use on nuclear reactors, spacecraft, nose tips, and various other leading edges.

It is another object of this invention to provide ceramic insulation tile having high temperature characteristics, lightweight, high tensile strength and capable of being formed into any desired shape.

It is a further object of this invention to provide ceramic insulation tile comprising siloxanes derived from the reaction of dialkoxy silanes and tetraalkoxy silanes, and preferably from the reaction of dialkoxy silanes and tetraalkoxy silanes, for use on space vehicles and other insulation applications, having improved high temperature characteristics, lightweight and high tensile strength.

These and other objects of this invention will become apparent from a further and more detailed description of the invention as follows.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a black oxidation resistant, lightweight amorphous high-temperature ceramic insulation comprising silicon, carbon and oxygen atoms and to the method for preparing said insulation which comprises the formation of a siloxane gel derived from the reaction of di- and tetraalkoxy silanes in a liquid medium such as water and/or alcohol to form a siloxane gel, followed by drying the gel at ambient pressure without using an autoclave, and subsequently heating or pyrolyzing the dried sponge gel, in an inert atmosphere, to form the black ceramic insulation. In one embodiment, the siloxane gel in various amounts of alcohol and water, is dried at ambient pressure to form a ceramic siloxane precursor. The ceramic siloxane precursor is subsequently pyrolyzed, in an inert atmosphere i.e. inert gas, to form the black ceramic insulation of this invention.

The insulation is characterized as having limited shrinkage in size, shape and configuration and to high-temperature resistance. Various amounts of solvent i.e. water, alcohol and mixture thereof in any ratio can be used to achieve the desired density and strength of the high-temperature oxidation-stable ceramic insulation.

For purposes of this invention, the preferred di- and tetrafunctional alkoxide reactants include the alkoxydes of silicon having two and four Si—O bonds, respectively. Particularly preferred silanes comprise a combination of silanes with tetra- and oxy functionality having the general formula Si(OR)₄ and (RO)₆—Si—R where R, R', R'' and R'' are the same or different and represent organic radicals of 1–12 carbons such as an alkyl, alkenyl,aryl or substituted radical of 1 to 12 carbons such as an alkyl, alkenyl or substituted radical of 1 to 12 carbons.

The hydrocarbons comprise carbon and hydrogen (—CH) which may be straight or branched chain, saturated or unsaturated radicals. In general, the number of carbon atoms in the hydrocarbon or organo groups range from 1–12 and preferably from 1–8 and more preferably 1–4 carbons e.g. 1–2 carbons such as methyl, ethyl propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, heptyl, etc., the isomers, and mixtures thereof and include the alkylvin or vinyl unsaturated groups such as vinyl, divinyl, propenyl, butenes, etc. and various mixture thereof in various ratios.

Specific examples of some of the preferred silanes useful for preparing the siloxane gels of this invention include the tetraalkoxy silanes such as tetramethoxy silane or tetraethyl silane. Some of the preferred dialkoxy silanes include the diethyldiethoxysilane (C₂H₅)₂Si(OC₂H₅)₂, diethyldiethoxymethoxy silane (C₂H₅)₂Si(OC₂H₅)₂[OCH₃], dimethyldiethoxysilane (CH₃)₂Si(OC₂H₅)₂, dimethylmethoxy silane (CH₃)₂SiOCH₃, diphenyldiethoxymethoxy silane (C₆H₅)₂Si(OC₂H₅)₂[OCH₃] and various combination thereof in any ratios.

The siloxane sol-gels of this invention are prepared by reacting the alkoxysilanes in the presence of an aqueous catalyst (up to about 10% e.g. 0.1 to 2.0%) by weight of the liquid medium) in an aqueous-alcohol or alcohol medium.

The weight ratio between the dialkoxy silane and the tetraalkoxy silane ranges from 1.0 to 0.1 part by weight of the tetraalkoxy silane to 2.0 part by weight of the dialkoxy silane and preferably from about 0.7 to 1.5 parts by weight.

The alcohol media insures that a homogeneous sol-gel is obtained. While it is convenient to use the lower alcohols such as ethanol, other lower aliphatic alcohols of 1 to 8 carbons e.g. 1 to 4 carbons may be used alone or in admixture in any ratio. Examples of the preferred alcohol media include methanol, ethanol, propanol, isopropanol, butanol, sec- and isobutanol, pentanol, and any mixture of the lower alcohols alone or with water in any ratio. Although the siloxane sol may be gelled by aging at ambient temperatures or by heating, it is preferred to catalyze gelation by the addition of a catalytic amount e.g. 0.1 to 2.0% by weight of a dilute mineral acid e.g. HNO₃, HCl, etc. or a base such as NaOH, KOH, ammonium hydroxide or a low molecular weight amine etc. to the reaction mixture. Mineral acids such as nitric acid or a base such as ammonium hydroxide are particularly useful as gelling agents. Gelation will occur at ambient conditions, but heating to temperatures of from about 40°–90°C is preferred also in addition to the use of the acid or base catalyst. After gelation, the gel is dried in an oven or at ambient conditions to form the siloxane precursor.

Vacuum drying (e.g., overnight at 70–100°C) is not necessary to insure that the gel does not shrink, significantly, prior to pyrolyzing the gel in an inert atmosphere.

In addition, the reaction mixture of this invention may contain small but effective amounts of at least one mono- or trialkoxy silane in combination with the di- and tetraalkoxy silanes, in the ratios of about 1.0 part by weight of the
In accordance with this invention, the insulation is formed by heating the dried white siloxane gel at temperatures ranging up to about 1500°C in an inert atmosphere. The inert atmosphere includes a vacuum or an atmosphere of one or more of the inert gasses, such as argon, nitrogen, helium etc. and various mixture thereof. Some specific examples of the mono- and trialkoxy silanes useful for preparing the siloxane gels of this invention include the alkyltrialkoxy silanes such as methyl trimethoxy silane \( \text{CH}_3\text{Si(OC}_2\text{H}_3)_3 \), ethyltrimethoxy silane \( \text{C}_2\text{H}_5\text{Si(OC}_2\text{H}_3)_3 \), methyltritylmethoxy silane \( \text{CH}_3\text{Si(OCH}_3\text{)}_3 \), and various monomethoxy silanes such as trialkylethoxy silanes and trialkylmethoxy silanes etc.

The ceramic insulation is formed by heating the dried sponge white siloxane gel at temperatures ranging up to about 1500°C in an inert atmosphere. The inert atmosphere includes a vacuum or an atmosphere of one or more of the inert gasses, such as argon, nitrogen, helium etc. In order to increase the strength of the ceramic insulation, after pyrolysis, the ceramic insulation or tile can be further fired at temperatures up to about 1500°C for about 10-60 min in air. To further increase the density of the ceramic insulation, a gel formed within two hours. The ceramic insulation materials e.g. ceramic insulation tiles in various temperature characteristics, light-in-weight, with high-strength and could be formed into the desired shape for various end uses.

The following Examples illustrate the preparation of the ceramic insulation materials e.g. ceramic insulation tiles in accordance with the process of this invention.

**EXAMPLE 1.**
Tetramethoxysilane (2.0 g) and dimethyldimethoxysilane (1.0 g) were mixed with 4.0 g of methanol and stirred. After adding 0.5 g, 1.0 N of ammonium hydroxide, the siloxane gel formed within 60 min. One piece of the air-dry gel was pyrolyzed at 1200°C in argon for one hour. This black ceramic insulation was stable at 1600°C in air.

**EXAMPLE 2.**
Tetraethoxysilane (2.0 g) and dimethyldiethoxysilane (1.0 g) were mixed with 6.0 g of ethanol and stirred. After adding 0.5 g of 0.5 N of sodium hydroxide, the siloxane gel formed within two hours. The air-dry gel was pyrolyzed at 1000°C for one hour. This black ceramic insulation tile was stable at 1700°C in air.

**EXAMPLE 3.**
Tetraethoxysilane (2.0 g) and dimethyldiethoxysilane (0.8 g) were mixed together with 5.0 g of ethanol. After several hours, 0.5 g of 0.5 N of ammonium hydroxide was added to the reaction and a gel formed within two hours. The
air-dry gel was heated at 1300° C in argon. The resultant black ceramic insulation was stable at 1700° C in air.

**EXAMPLE 4.**

Tetramethoxysilane (2.0 g) and dimethyldiethoxysilane (1.5 g) were mixed together with 6.0 g of ethanol and stirred for several hours. After adding 0.5 g of 0.5 N sodium hydroxide, a siloxane gel was formed. Pyrolyzing the air-dry gel at 1100° C in argon resulted in a black ceramic insulation tile which was stable at 1700° C in air.

**EXAMPLE 5.**

Tetramethoxysilane (2.0 g), methyltrimethoxysilane (0.5 g) and methyltrimethoxysilane (1.0 g) were mixed with 6.0 g of methanol and stirred at room temperature. After adding 0.5 g of 1.0 N of ammonium hydroxide, a siloxane gel was formed within 60 min. One piece of the air-dry gel was pyrolyzed at 1200° C in argon for one hour. This black ceramic insulation was stable at 1600° C in air.

**EXAMPLE 6.**

Tetraethoxysilane (2.0 g), dimethyldiethoxysilane (1.0 g) and trimethylethoxysilane (0.1 g) were mixed with 5.0 g of ethanol and 0.1 g of 0.1 N nitric acid under stirring for 1-20 hours. After adding 1.0 g of 1.0 N of ammonium hydroxide to the reaction mixture, a siloxane gel was formed within 60 min. Once piece of the air-dry gel was pyrolyzed at 1100° C in argon for one hour. This black ceramic insulation was stable at 1600° C in air.

It is understood that various other embodiments and modifications in the practice of the invention will be apparent and can be made by those skilled in the art without departing from the scope and spirit of the invention as set forth in the appended claims.

The invention claimed:

1. A process of preparing an oxidation-stable, high temperature, porous ceramic insulation which comprises reacting in a liquid medium effective amounts of (a) at least one tetraalkoxy silane having the formula:

   \[ \text{Si(OR)}_4 \]

   wherein \( \text{R}^1 \) is a saturated or unsaturated organic radical having 1 to 12 carbons and (b) at least one dialkoxy silane having the formula:

   \[ \text{(R'O)}_2\text{—Si—(OR)}_2 \]

   wherein \( \text{R}^2 \) is a saturated or unsaturated organic radical having 1 to 12 carbons and \( \text{R}^4 \) and \( \text{R}^6 \) are alkyl radicals of 1-4 carbons, and the ratios in the reaction mixture are about 1.0 part by weight of the tetraalkoxy silane to about 0.7 to 1.5 parts by weight of the dialkoxy silane, and the siloxane gel is dried at temperatures ranging from about 100° C to about 150° C.

2. The process of claim 1 wherein the reaction ratio of the tetraalkoxy silane to the dialkoxy silane is about 1.0 part by weight of the tetraalkoxy silane and the siloxane gel is dried at temperatures ranging from about 100° C to 150° C.

3. The process of claim 2 wherein the reaction ratio of the tetraalkoxy silane to the dialkoxy silane is about 1.0 part by weight of the tetraalkoxy silane, and the siloxane gel is dried at temperatures ranging from about 100° C to 150° C.

4. The process of claim 2 wherein \( \text{R}^1 \) and \( \text{R}^2 \) are alkyl radicals of 1 to 8 carbons and \( \text{R}^4 \) and \( \text{R}^6 \) are alkyl radicals of 1 to 8 carbons.

5. The process of claim 2 wherein \( \text{R}^1 \), \( \text{R}^2 \), \( \text{R}^4 \), and \( \text{R}^6 \) are alkyl radicals of 1 to 4 carbons.

6. The process of claim 2 wherein the liquid medium comprises alcohol.

7. The process of claim 2 wherein the liquid medium comprises water.

8. The process of claim 2 wherein the liquid medium comprises a mixture of alcohol and water wherein the ratio of water to alcohol is about 1.0 part by weight of water to 1-100 parts by weight of alcohol.

9. The process of claim 6 wherein the alcohol comprises at least one aliphatic alcohol having 1 to 8 carbons.

10. The process of claim 8 wherein the mixture of alcohol and water contains a catalytic amount of at least one catalyst.

11. The process of claim 10 wherein the catalyst is an acidic catalyst.

12. The process of claim 10 wherein the catalyst is a basic catalyst.

13. The ceramic insulation obtained by the process of claim 1.

14. The ceramic insulation obtained by the process of claim 2.

15. The ceramic insulation obtained by the process of claim 8.

16. The process of claim 1 wherein the reaction between the tetraalkoxy silane and the dialkoxy silane contains effective amounts of at least one alkyl trialkoxy silane having the formula:

   \[ \text{R}^5\text{—Si(OR)}_3 \]

   wherein \( \text{R}^5 \) is a saturated or unsaturated alkyl radical of 1 to 12 carbons and \( \text{R}^8 \) is an alkyl radical of 1 to 12 carbons.

17. The process of claim 1 wherein the reaction between the tetraalkoxy silane and the dialkoxy silane contains at least one alkyl monoalkoxy silane having the formula:

   \[ \text{R}^5\text{—Si—(OR)}_2 \]

   wherein \( \text{R}^7 \) is a saturated or unsaturated alkyl radical of 1 to 12 carbons and \( \text{R}^8 \) is an alkyl radical of 1 to 12 carbons.

18. The process of claim 16 wherein \( \text{R}^5 \) and \( \text{R}^8 \) are alkyl radicals of 1-4 carbons and the ratios in the reaction mixture are about 1.0 part by weight of the tetraalkoxy silane to about 0.1 to 2.0 part by weight of the dialkoxy silane to about 0.01 to 0.5 part by weight of the trialkoxy silane.

19. The process of claim 17 wherein \( \text{R}^5 \) and \( \text{R}^8 \) are alkyl radicals of 1-4 carbons and the ratios in the reaction mixture are about 1.0 part by weight of the tetraalkoxy silane to about 0.1 to 2.0 part by weight of the dialkoxy silane to about 0.01 to 0.5 part by weight of the alkyl monoalkoxy silane.

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