Title: Aerogel - Tile Composites toughen a Brittle Superinsulation

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Abstract

Pure aerogels, though familiar in the laboratory for decades as exotic lightweight insulators with unusual physical properties, have had limited industrial applications due to their low strength and high brittleness. Composites formed of aerogels and the ceramic fiber matrices like those used as space shuttle tiles bypass the fragility of pure aerogels and can enhance the performance of space shuttle tiles in their harsh operating environment. Using a layer of aerogel embedded in a tile may open up a wide range of applications where thermal insulation, gas convection control and mechanical strength matter.

Introduction

A new composite made by partly filling spacecraft insulation tiles with a layer of aerogel springboards off the advantageous thermal and physical properties of aerogels, but maintains the strength and other proven advantages of the space shuttle tiles. Pure aerogel is an outstanding lightweight thermal insulator but it is too fragile for many uses. This composite is the first form of aerogels that could be coated, cut, machined, drilled and attached to a surface, making it useful in the harsh operating conditions experienced by spacecraft insulation and in other industrial applications. This composite was developed as a result of an investigation into enhancing aerogel strength for robust superinsulation.

Pure aerogels are an exotic class of materials, with remarkable and very useful properties, but they remain in search of large-scale applications. They include the lightest or lowest density solid materials known. The thermal conductivity of pure aerogels can be extremely low and varies over a wide range, as a known function of temperature and density. The index of refraction can be very close to unity, which is that of vacuum or air. Being porous materials with extremely small pores and very high surface areas, aerogels offer potential filters and catalytic surfaces. Aerogels have long been used in particle physics, more recently as cosmic dust collectors, but their use as an insulator has been severely limited by its fragility, as well as the tendency of hydrophilic aerogels to degrade after absorbing moisture from the air. Pure aerogels are light but weak.

Pure Aerogels have been available for decades but uses have been limited by several problematic properties which are currently under attack by researchers. Invented in 1931 by Kistler at the College of the Pacific in Stockton, Ca - aerogels are formed from a gel structure with the liquid phase replaced by air. However, simple air-drying could not be used. Inside the gel, surface tension at the liquid-vapor interface exerted sufficient force
over the small radius pores to destroy the gel framework. The gel structure only remained intact when the mother liquid was removed by supercritical drying – heating the gel under pressure until the liquid changed to a vapor without the formation of a meniscus between the liquid and vapor phases. The original production method took weeks. There is a legendary and instructive story of a graduate student’s nervous breakdown when he was assigned to produce a large number of samples and calculated how long it would take to do so. Upon recovery, the graduate student made a significant breakthrough in production methods, reducing production time from weeks to days. Supercritical drying with high-pressure alcohol is efficient but hazardous. LBL developed a much safer and less costly production method, drying the gel with supercritical carbon dioxide rather than supercritical alcohol.

Low-density aerogels were first made at LLNL in 1980’s, and new records for low density continue to be made. Organic aerogels were developed in the last decade at LLNL. Less hazardous and less expensive production methods to eliminate the supercritical drying step were developed at UNM and other facilities and continue to be explored and improved.

Space shuttle tiles are an open framework of ceramic fibers sintered together at limited contact points, forming a well-tested and proven insulation which is tough, refractory, which can be machined, coated and adhered to a spacecraft’s surface. The fibers used to form the tiles are mostly a mixture of silicon and aluminum oxides. A typical shuttle tile is 15 cm (six inches) square. The initial problems of tiles failing to adhere to a spacecraft’s surface during the early history of spaceflight have long been resolved, and a typical space shuttle tile lasts many flights and is only replaced when surface damage goes beyond acceptable limits.

In this composite, aerogel is infused into space shuttle tiles, either completely filling the tile or filling a layer. Figure 2 illustrates methods of forming the layer inside the tile. For spacecraft insulation, the layer is sized at the maximum thickness which will not melt from reentry heating. That is, the predicted heating profile when the spacecraft slows itself down by friction from a planet’s atmosphere is used to locate the isotherms corresponding to the melting temperature of the aerogel. Layers below this isotherm are cooler than the melting temperature and so will not melt. Filling some or all of the pore spaces of a tile with aerogel lowers the conductivity of the tiles, which are already an excellent insulator, without sacrificing the strength and other required properties of the tiles. Figure 3 shows a visualization of the composite in use on a spacecraft.

This composite is the first form of aerogels that could be machined, hammered on, glued and coated, making it useful for our and other industrial applications. The spaces between the fibers inside a standard spacecraft tiles are less than a millimeter wide. The aerogel-phase of the composite almost completely blocks gas flow and the simultaneous transport of heat by gas flow. Since conduction through the solid is also very low, the overall conductivity is decreased to that of a tile in vacuum, that is, without air present in the pores. This insulation reduces gas transport to a diffusion-controlled process – the slow meandering Brownian motion of molecules through the pores of the material.
Application as multi-use insulation

The aerogel-tile composite was designed for improved insulation for spacecraft and reusable cryogenic tank insulation. Currently, cryogenic fuel tanks are insulated with organic closed-cell foam and are only used once. Cost reduction demands the development of reusable cryogenic insulation. The aerogel/tile is expected to function as a multi-use insulation, to protect spacecraft from high heating as well as extreme cold, since the extremes of temperature are experienced at different times during a mission. That is, a reusable cryogenic fuel tank experiences both a cold soak and a heat soak at different phases of a flight. The cold cycle starts during groundhold, during cryogenic fuel tanking. The problem during cold soak is to prevent moisture and oxygen condensation on tank wall. The aerogel insulation controls mass transport by extremely reduced permeability, as well as heat transfer. During the hot cycle phase of a flight mission - after the fuel is used and tank reenters the atmosphere, reentry heating. The aerogel in the composite tile loading lowers the conductivity of the tile by depressing convection, by preventing gas flow through the tile. The aerogel can also be used to distribute opacifiers – materials which absorb and reradiate radiation, closing the infrared window commonly seen in silica aerogels. In addition, extremely lightweight tiles can serve as the matrix for the aerogels, trading off on the improved conductivity of the tiles, and utilizing recent advances in tile manufacture.

Space shuttle tiles have a higher conductivity in air than in vacuum, because the gas transports a significant amount of energy across the tile. Adding the aerogel to depress the contribution of gas to heat transfer is like having a chunk of solid vacuum where you need it. Tests are underway to characterize the material response to repeated cooling and heating, to identify technical problems and develop solutions as required. Key problem areas already resolved include restricting moisture absorption by the normally hydrophilic aerogel materials, ensuring good adhesion between the tile fibers and the aerogel phase, and preventing thermal stresses from impacting the aerogel matrix.

High temperature and environmental testing of aerogel-tiles has been conducted at NASA Ames Research Center for several years. The key tests were a series of atmospheric entry simulations undertaken to demonstrate the response of the material to the heating cycle experienced by spacecraft insulation. The composite performed as anticipated during these tests. In this application, heating is intense but of short duration. As usual, the thickness of the insulation is determined to keep key areas, here the inner mold line at a moderate temperature. As a result, the outer surface becomes extremely hot, but the maximum temperature experienced inside the insulation decreases moving away from the hot surface. Isotherms of maximum temperatures can be defined for all positions inside the insulation. The position experiencing sufficient heating to melt or sinter the aerogel phase determines the boundary between where the aerogel will survive unchanged. That is, in regions where the temperature was held long enough and high enough to sinter or melt the aerogel, it sintered, forming a coating on the tile’s fibers. In regions that did not experience sufficient heating to sinter the aerogel, the aerogel and the composite remained unchanged.
Figure 4 illustrates this reduction in thermal conductivity two silica aerogel - tile composite material samples under atmospheric pressure, compared to data for the tile under vacuum and at atmospheric pressure, showing the aerogel-tile composite acts like a tile under vacuum. The aerogel phase in the composite successfully reduce energy transport by convection without simultaneously greatly increasing heat transfer through conduction or radiation. Because the aerogel phase has extremely small pores, typically on the order of 50 nanometers, gas convection, which is energy transport by the motion of a gas through the material, is reduced to a minimal value. The aerogel has a much lower thermal conductivity than the porous ceramic fiber material matrix used on spacecraft, so the thermal conductivity of the composite is not greatly increased.

Industrial Applications

Aerogels have already found applications as radiation detectors, cosmic dust collectors, and more recently using carbon aerogels as capacitors and for chemical reactors. Many insulation uses have been explored, particularly for the most transparent silica aerogels. The aerogel-tile material could be used in many commercial products that require mechanically tough super-insulation, such as catalytic converters for cars or specialty refrigeration units. This new material could be used for furnace insulation, and, to insulate against extremely cold temperatures, for liquefied gas transport containers used to transport liquid carbon dioxide, nitrogen and oxygen. Uses for catalytic reactions on the microporous surface may be expanded using this toughened material.

Although this is envisioned as an insulation material, any totally new material can be expected to find uses not originally planned as the properties and advantages of the new materials define a new niche.
Figures
Figure 1

PHOTO - AEROGEL ON A TILE

Figure 2 - Processing Methods

PARTLY RESIN-FILLED MATRIX

AEROGEL PRECURSOR SOLUTION

IMPREGNATE MATRIX,
GEL IN PLACE,
DRY AEROGEL INSIDE MATRIX

PURE MATRIX

ATTACH TO SPACECRAFT,
USE REENTRY HEATING
TO SINTER BACK AEROGEL
IN TOP LAYER
Figure 3
Sketch of Aerogel / Tile composite

After reentry heating sinters back Aerogel, this cross-section of insulation shows the two-layer composite.

Figure 4
Graph of conductivity vs. Temperature of pure Tile and Aerogel / Tile for vacuum and 1 atm pressure.
FIGURE 2

TEMPERATURE (°C)

0 100 200 300 400 500

CONDUCTIVITY IN TRANSVERSE DIRECTION

CURRENT INVENTION - AEROGEL COMPOSITE
+ 0.12 COMPOSITE TRANSVERSE + 1 ATM
PURE TILE WITHOUT AEROGEL
--- ACTUAL TRANSVERSE + 1 ATM
II ACTUAL TRANSVERSE + 0.02 ATM

TILE AT 1 ATMOSPHERE

TILE UNDER VACUUM

FIGURE 2