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ABLATIVE ANTENNA WINDOW COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

A composition comprising boron nitride fibers embedded in a resin matrix can be molded to form an article which exhibits good ablative properties, does not char, and has good electromagnetic transmission from low to high temperatures, and when degrading at high temperatures. The composition comprises about 60–95 percent resin, preferably a polyfluorocarbon polymer. Additional powdered or fibrous fillers can be added—boron nitride, quartz, silica, alumina, zirconia, magnesia, beryllia, glass, aluminum silicate, titania, barium titanate, calcium titanate, or strontium titanate. The article is useful as an antenna window in high speed aeronautical and aerospace vehicles subject to aerodynamic heating during passage through the atmosphere.

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without payment to me of any royalty thereon.

DESCRIPTION OF THE INVENTION

The invention deals with ablative compositions suitable for use in electromagnetic-transparent antenna windows in ultra high speed aeronautical and aerospace vehicles such as hypersonic gliders and space vehicles designed for re-entry into the atmosphere. Specifically, the invention deals with substantially non-charring compositions comprising boron nitride fibers embedded in a substantially non-charring resin matrix.

The term "substantially non-charring," as used herein means that there is no charring at all or that the proportion of residual char (usually less than about 5 percent) does not interfere significantly with the electromagnetic transmission properties of the composition.

It is frequently necessary to transmit information or signals to, or from, manned and unmanned flight vehicles. These might be for the purpose of destruction, flight path changes, transmission of scientific data, and the like. For example, an aerospace vehicle might transmit scientific information to a ground based receiver and to a satellite-based receiver in the range of X-band or other very high frequencies. Such a vehicle, therefore, requires that a portion of its containing wall be electromagnetic-transparent; that is, that it contain an antenna window capable of transmitting electromagnetic signals from inside to outside, and from outside to inside, the vehicle.

Antenna windows are generally flush mounted on the external surface of a flight vehicle and hence must be capable of withstanding the unique environmental conditions which such vehicles encounter. One such condition arises when, for example, the surface of an aerospace vehicle antenna window encounters the atmosphere upon re-entry, becomes extremely hot, and degrades thermally. If the composition of the antenna window is not satisfactory, thermal degradation can result in (1) poor ablative performance and a resulting "burn through," or (2) the production of degradation products which destroy or

severely restrict the window's electromagnetic transmission properties. In the latter case, communication between the vehicle and the ground cannot be carried out during, and following, such thermal degradation.

The use of a homogeneous bulk ceramic material has been suggested and such compositions have been used in antenna windows on high speed entry vehicles and devices. The ceramic can be glass, alumina, quartz, boron nitride, or a like material possessing moderate thermal stability and suitable electrical properties for radar transmission. These ceramics, however, have behaved poorly in high speed entry vehicles and in flight speeds over 15,000 feet per second because of (1) thermal shock failure, (2) occasional spallation, (3) having a finite melting or degradation point which limits maximum service temperatures, (4) thermal stresses which limit the incident heating rate, and (5) being difficult to attach to the remainder of the vehicle.

It has been suggested that ablative fiber-containing plastics be used to make antenna windows when the latter is to be subjected to environmental temperatures and incident heating rates which preclude the use of bulk ceramics. Thus, fiber-reinforced polytetrafluoroethylene; for example, polytetrafluoroethylene reinforced with 30 percent by weight silica fiber (acid leached glass) or reinforced with 25 percent by weight aluminum silicate fiber; has been used with only moderate success. One disadvantage of prior art fiber-resin composites has been the mismatch in linear ablative rates of their components, which mismatch results in uneven erosion of the surface and a resulting early change in the air boundary layer from laminar to turbulent (inducing unnecessarily higher surface heating at an earlier time in the flight). A second disadvantage results from relatively high linear and mass ablation rates. A high mass ablation rate, or erosion rate, can influence the dynamics of the vehicle in an undesirable and unpredictable manner. A third disadvantage results from the melting of the ceramic fiber which tends to agglomerate into droplets and impact on, and damage, downstream portions of the vehicle. Such droplets, or partially molten material, may also be forcibly injected into the boundary layer in a manner to lead to lower thermal efficiency of the window material.

The requirements for a good ablative antenna window composition are therefore numerous, demanding, and difficult to meet. Some of the requirements are: (1) a high radar transmission with minimum energy attenuation, scattering, or reflection; (2) substantially complete maintenance of such transmission characteristics over temperature ranges from cryogenic to thermally degrading temperatures; (3) a loss tangent of less than 0.01; (4) good isotropic properties; (5) low thermal conductivity; (6) high thermal stability; (7) high ablative heat shielding; (8) low density; (9) low permeability; (10) compatibility with adjacent vehicle structure for effective assembly; (11) degradation to gaseous products which are ionized with great difficulty or are electrophilic; (12) a dielectric constant in the range of 1–5; (13) capability of being molded or otherwise formed by known fabrication methods; (14) composed of inexpensive, non-strategic materials; and (15) composed of non-toxic materials.

OBJECTS

It is an object of my invention to provide a composition capable of being molded into an improved ablative antenna window suitable for use in ultra high speed aeronautical and aerospace vehicles.

It is a further object to provide an article which has superior ablative characteristics, does not char substantially, and which has good electromagnetic transmission

characteristics while undergoing, and following, high temperature surface degradation.

It is a further object of my invention to provide a composition which is superior to those of the prior art in meeting the above stated desirable requirements for ablative antenna window compositions.

It is a still further object to provide a composition which is sufficiently pliable to be readily formed in a mold under compression.

I have now found that the foregoing and related objects can be attained in a composition comprising boron nitride fibers in a substantially non-charring resin matrix. The resin complex preferably makes up from about 60 to about 95 percent by weight of the composition. At least one additional filler can be used and can be selected from the group consisting of boron nitride, quartz, silica, alumina, zirconia, magnesia, beryllia, glass, aluminum silicate, titania, barium titanate, calcium titanate, and strontium titanate. Quartz fiber, alumina in the form of "whiskers," and boron nitride powder are especially valuable. It is to be understood that the selected filler is to be used in either a powdered or fibrous form. Boron nitride, as a filler, is used in its powdered form for the reason that the compositions of the invention all contain boron nitride fiber as an essential element thereof.

Boron nitride fiber is available commercially as loose fiber or as a woven fabric and can be used in either form. A typical fiber is about 10 to 15 inches long, about 5–7 microns in diameter, has a density of about 1.8–2.0 grams per cc., dissociates at 4800° F., has a dielectric constant of about 4.3–5.2, has a high dielectric strength and electric resistivity, has a tensile strength of about 200,000 pounds per square inch, has an elastic modulus of 13,000,000 pounds, is nonpermeable, is white in color, and is 99 percent pure. Boron nitride fibers are non-wetting and therefore were not expected to form mechanically strong plastic composites. I was surprised to discover that non-charring polymers, especially the polyfluorocarbons, are completely compatible with boron nitride fibers to form a dense solid composite mass.

DETAILED DESCRIPTION

In the preparation of the ablative antenna window of the invention I usually treat commercially available boron nitride fibers as follows. The fibers are dried to a constant weight by storing them in a desiccator or by holding them in a vacuum oven at, for example, 150° F. The fibers are then broken to relative short lengths. A length of about one millimeter is suitable. I usually break the fibers by "blending" them in a blender for about 15 minutes, the fibers being covered with acetone to keep them from clumping.

The acetone-fiber slurry may then be placed in a glass dish, or the like, and the acetone allowed to evaporate. Residual acetone can also be removed by placing the resulting fiber mat in a vacuum oven and slowly heating it to about 100° F.

The fiber mat may then be mixed with the resinous matrix material in a number of ways. For example, the fiber mat may be mixed, in a mechanical mixer, with a suitable proportion of a polymer suspension. A particularly useful substantially noncharring polymer is polytetrafluoroethylene, and a suitable suspension is a 60 percent solids dispersion comprising 0.05–0.5 micron particles and a water carrier. Substantially non-charring fluorocarbon polymers and copolymers are especially suitable and are preferred for use in the composition of the invention. Specifically preferred resins are polytetrafluoroethylene, polytrifluoroethylene, the copolymer of tetrafluoroethylene and trifluoroethylene, and the copolymer of tetrafluoroethylene and hexafluoropropylene.

After thoroughly dispersing the boron nitride fibers in the polymer suspension, the mixture may be dried in a vacuum oven at a reduced pressure and at a temperature of about 250° F. Alternatively, the slurry may be evenly deposited on a suction screen or filter, the free water being removed by suction and the residual water being removed in a vacuum oven at about 250° F. In this manner, a thin preform mat composed of short boron nitride fibers in a plastic matrix is formed. Such preforms, if the proportion of plastic is between about 60 and about 95 percent by weight, are sufficiently pliable to easily conform to the configuration of a mold. A convenient way of molding an antenna window, or other object, is to cut pieces of the preform and pile them, layer upon layer, in the mold until a desired thickness is reached. Molding may be carried out in conventional molds under, for example, about 5000 p.s.i. pressure. The mold may be heated to a maximum temperature of about 700° F., held at that temperature for about 20 minutes, and then slowly cooled to room temperatures. Upon release of the mold pressure, the formed solid article can be removed from the mold.

In an alternative embodiment of the invention, I mix the short boron nitride fibers with a finely divided polymer; for example, a polytetrafluoroethylene powder. The polymer and fibers are thoroughly mixed in a suitable mechanical mixer and the mixture is then dried. Suitable drying of the mixture can be carried out in a vacuum oven at 250° F. The dry mixture is then put into a mold and compression molded at 2000 p.s.i., for example. The mold contents may be heated to a maximum temperature of 700° F. and then held there for about 20 minutes (or a time suitable for the sintering of the polymer). The mold may then be cooled, the pressure released, and the molded article removed therefrom.

I have found that when the resin matrix comprises about 60–95 percent and boron nitride fibers comprise the balance (that is, about 5–40 percent) of the molded article, the latter transmits a high percentage of incident electromagnetic wave energy in the frequency range now used in electromagnetic communications (for example, X-band and other very high frequencies). More important, this performance feature is substantially maintained when a surface of such article is being thermally degraded. The articles, further, are characterized by (1) low density, (2) a dielectric constant between 2.2 and 3.5 and dielectric properties which do not change substantially up to about 500° F., (3) low thermal conductivity, (4) high thermal stability, (5) high ablative heat shielding, (6) non-charring at high temperatures, (7) degrades to gaseous products which are ionized with great difficulty or are electrophilic, (8) low permeability, and (9) a loss tangent of less than 0.01.

In addition to the foregoing valuable electrical and thermal properties, the molded object of the invention is (1) made of non-expensive, non-strategic materials, (2) non-toxic, (3) readily formed by well known molding and other fabrication techniques, (4) readily integrated with adjoining vehicle structures, and (5) has a good storage life.

Fillers may be used with advantage in the resin-boron nitride fiber composite of the invention. Thus, there can be added at least one filler selected from the group consisting of boron nitride, quartz, silica, alumina, zirconia, magnesia, beryllia, glass, aluminum silicate, titania, barium titanate, calcium titanate, and strontium titanate. As indicated above, the fillers are used in powdered or fibrous form and boron nitride, when used as a filler, is used in powder form. Boron nitride powder, when used with boron nitride fibers, is a preferred filler and is used preferably in a proportion of about 2–10 percent by weight of the total filler and boron nitride fiber mass to yield a more highly packed molded article with more uniformity of ablation. Quartz fibers, also a preferred filler, may be used with boron nitride fibers in proportions of 5–50 percent by weight (for example) of the total filler-boron nitride fiber mass to yield an article which is relatively stronger, has significantly superior ablative efficiency, and has significantly superior dimensional stability during very high temperature of exposure. Alumina whiskers, when

used with boron nitride fibers, can be used in proportions of about 5–30 percent (for example) of the total filler-boron fiber mass to yield a highly packed molded article of relatively high strength and high elastic modulus values.

EXAMPLE 1

Boron nitride staple fibers (from the Carborundum Company, Niagara Falls, N.Y.) were dried to a constant weight in a 150° F. vacuum oven. The dry fibers were then transferred to a high speed blender, covered with chemically pure acetone, and "blended" over a period of 15 minutes to an average length of about one millimeter. The resultant slurry was then transferred to a glass dish and the acetone was permitted to evaporate. The fiber mat was then placed in a vacuum oven and slowly heated to 100° F. to remove residual acetone.

A portion of the fiber mat (120 grams) was placed in a mechanical mixer and was mixed therein with 1550 grams of dispersed polytetrafluoroethylene, the latter being added in the form of an aqueous suspension containing 60% solids. When the boron nitride fibers were thoroughly dispersed in the suspension, the mixture was evenly deposited on a suction filter. Most of the water of the suspension was removed in the filtration, the remainder being removed by drying at 250° F. in a vacuum oven for about two hours. The resulting preform was composed of short chopped fibers intimately coated with polytetrafluoroethylene homopolymer and was sufficiently pliable to conform easily to the configuration of a mold. The preform fiber mat was cut into a number of pieces which were placed layer upon layer in a mold until the desired thickness was reached. A pressure of 5000 pounds per square inch was applied and the mold was heated slowly to a maximum temperature of 700° F. The temperature was held at 700° F. for 20 minutes and was then permitted to cool slowly to room temperature. The pressure was then slowly reduced to ambient and the formed article was removed from the mold.

The resulting article, comprising about 7 percent by weight boron nitride fiber and 93 percent polytetrafluoroethylene was rigid and had the following properties:

Density	2.16 grams per cc.
Water absorption	0.38 percent after one hour in boiling water.
Water loss	0.59 percent after 20 hours drying at 160° F.
Dielectric constant	2.28 (when tested at 9.35×10^9 cycles per second) and relatively constant dielectric properties from room temperature to 500° F.
Loss tangent	0.003 when tested at 9.35×10^9 cycles per second.
Thermochemical heat of ablation	2400 B.t.u. per pound at test air enthalpies of 2900 B.t.u. per pound and incident cold wall heating rate of 300 B.t.u. per square foot per second.
Linear mass ablation rate	Substantially less than a comparable aluminum silicate fiber filled polytetrafluoroethylene.

The improved ablative performance of the boron nitride filled polytetrafluoroethylene was attributed primarily to the fact that both fiber and resinous matrix sublimed. The resinous matrix, upon the application of heat, did not char, but decomposed (or depolymerized) to volatile lower molecular weight gaseous products. The subliming boron nitride also contributed greatly to the ablative efficiency of the molded composites, its heat of ablation being between 5100 and 16,300 B.t.u. per pound (depending upon the specific environmental conditions). The combined heat absorption by sensible temperature rise, by phase transformation, and by vapor blocking by both matrix and fiber led to a high thermal efficiency. Of particular significance to the invention was the fact that there was no charring of the composite during ablative degradation and hence there were no residual carbon deposits on the ablating surface to interfere with radar energy transmission through the material.

EXAMPLE 2

Short boron nitride fibers (80 grams) were prepared by drying to a constant weight, being subjected to the action of a blender while covered with acetone, and being freed from acetone (as described in Example 1). The resulting relatively dense fiber mat was then mechanically broken up into a "fluffed," relatively loose mat. The latter mat was mixed and stirred with 120 grams of finely divided solid polytetrafluoroethylene (cryogenically ground under liquid nitrogen). The fiber-polymer mixture was then transferred to a V-blender in which it was mixed for two days. The resulting mix was then thoroughly dried in a vacuum oven at 250° F. for four hours.

The resulting dry fiber-polymer mixture (60 percent polymer) was then put into a mold in which it was compression molded at 2000 p.s.i. The material was then heated in the mold to a maximum temperature of 700° F., held at that temperature for 20 minutes in order to insure proper sintering, and then cooled to 200° F. The pressure in the mold was released when the temperature reached 200° F. and the formed article was removed from the mold. Its properties were comparable to those of the formed article of Example 1.

EXAMPLE 3

Example 1 was repeated except that, during the stirring of the acetone-covered boron nitride fibers in the blender, 8 grams of powdered boron nitride powder (high purity fine grade, 15 micron size from the Carborundum Co., Refractories and Electronics Division, Latrobe, Pa.) were slowly added and dispersed within the fibrous mass. The subsequently formed article (as in Example 1) was substantially identical to the article of Example 1 except that the boron nitride powder containing product was denser and exhibited a more uniform ablation.

EXAMPLE 4

Example 1 was repeated except that, in place of the aqueous polytetrafluoroethylene, I used an aqueous suspension comprising a copolymer of polytetrafluoroethylene and hexafluoropropylene as the plastic matrix material. The latter copolymer has better melting and flow characteristics than the polytetrafluoroethylene homopolymer. A preform was formed as in Example 1 and the preform was charged to a mold. The preform was heated slowly to 500° F. for 30 minutes to release additional volatiles while under slight contact pressure. The mold was then heated to 650° F. for 20 minutes under a pressure of 1000 p.s.i. The temperature was then lowered to 200° F., the pressure released, and the rigid article removed. The properties of the formed product were substantially identical to those of the product of Example 1.

EXAMPLE 5

Example 1 was repeated except that 60 grams of quartz fibers were mixed with 60 grams of boron nitride fibers prior to subjecting the fibers to the action of the blender. The resulting dry chopped fibers were then mixed with 1550 grams of polytetrafluoroethylene homopolymer in the form of an aqueous suspension. The quartz fibers were pure fused silica filaments (Astroquartz Type 300½, No. 9705 braiding yarn sold by J. P. Stevens and Company,

New York, N.Y.). The resulting molded product was similar to that of Example 1 but had greater strength and had a significantly increased ablative efficiency and dimensional stability during very high temperature exposure.

EXAMPLE 6

Example 5 was repeated except that high strength alumina whiskers (from Thermokinetics Fibers Inc. of Nutley, N.J.) were used instead of the quartz fibers. The molded composition comprised 2 percent alumina whiskers, 10 percent boron nitride fibers, and 88 percent polytetrafluoroethylene, and was characterized by high strength, high elastic modulus, a relatively denser composite, and a relatively better packed composite than obtainable with filament fillers other than alumina whiskers.

It is to be understood that the foregoing examples and description are for the purposes of illustration only, and that various changes may be made therein without departing from the spirit and scope of the invention.

I claim:

1. A composition of matter suitable for use in an ablative antenna window for high speed aeronautical and aerospace vehicles, said composition comprising 5–40% by weight of boron nitride fibers in 60–95% by weight of a matrix comprising a polyfluorocarbon resin selected from the group consisting of polytetrafluorethylene, polytrifluoroethylene, the copolymer of tetrafluorethylene and trifluoroethylene, and the copolymer of tetrafluoroethylene and hexafluoroethylene.

2. The composition according to claim 1 wherein said composition also contains at least one filler selected from the group consisting of (a) powdered boron nitride, and (b) powdered or fibrous quartz, silica, alumina, zirconia, magnesia, beryllia, glass, aluminum silicate, titania, barium titanate, calcium titanate and strontium titanate in the amount of 5–50% by weight of the total filler and boron nitride fiber mass.

3. The composition of claim 2 wherein said filler is quartz fibers in the amount of 5–30% by weight of the total filler and boron nitride fiber mass.

4. The composition of claim 2 wherein said filler is alumina whiskers in the amount of 5–30% by weight of the total filler and boron nitride fiber mass.

5. The composition of claim 2 wherein said filler is powdered boron nitride in the amount of 2–10% by weight of the total filler and boron nitride fiber mass.

References Cited

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