Current status and trend of functional composites in aerospace applications

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Abstract: A review of the current status and trend of advanced functional composites for aerospace applications is presented in this paper. It covers an overview of the various types of functional composites in different application areas. Special emphasis is put on thermal protection functional composites in aerospace applications, including the thermal protection system and materials, the thermal ablative composites, the gradient composites and their compositions, functional mechanism and applications. Finally, the development trends are discussed. In general, the functional composites are developed in the direction of high performance, multiple functions and low-cost.

Key words: advanced functional composites; aerospace applications; thermal protection; review

CLC number: TB334; V258^{+}.3 **Document code:** A **Article ID:** 1673-1379(2012)02-0123-06

DOI: 10.3969/j.issn.1673-1379.2012.02.002

1 Definition of advanced functional composites and their classification[1]

Functional composite materials can be defined as a kind of material system containing two or more different phases in different compositions and forms on a macroscopic scale, including a continuous phase called the matrix, such as polymers, metals and ceramics matrices, and another phase of the functional agent in dispersed states, such as fibers, particles and whiskers, both of which are called the composite constituent materials or constituents in the composite technical terminology. The functional composites can offer not only the high enough mechanical strength and stiffness, but also some special functions, such as those in electrical, magnetic, optical, acoustic, thermal as well as biochemical applications.

The advantages of functional composites can be summarized as follows:

1) Designable functionalities and properties. The functional composites can be designed for different functional behaviors and functional degrees by selecting different types of constituents and different compositions to meet the different application requirements.

2) Short developing cycles. For a functional composite, the total developing cycle is much shorter from the beginning investigation to the final industrial application, than for a composite structure, especially, for aerospace structures, which usually takes 10~15 years before a successful application.

3) High additional economical values. Compared with structural composites, the performance to price ratio per unit mass material is much higher, which shows a good prospect in a wide range of applications.

4) Small production scale and a large number of varieties. In most cases, functional composites are in small production scales, but their products can be available in a large number of varieties.

5) Applicable for special areas. In many applications, functional composites can offer a unique function or some characteristics that other materials cannot provide. For example, the thermal ablation composite is a kind of unique functional material used for spacecraft and space vehicle thermal protection.

Functional composites can be divided into several major categories according to their application areas, as listed in Table 1.

Table 1 Classification and applications of functional composites

Functional items	Classification of composites	Major applications
Electrical Function	Conductive composite	Weak current switch, corrosion-resistant electrode
	Piezoelectric composite	Sonar, hydrophone biological sensors
	Electromagnetic shielding composite	Electronic devices shielding
	Wave transmitting composite	Aircraft radars and antenna cover
	Wave absorption/stealthy composite	Aircraft and missile skins
	Positive temperature Coefficient （PTC） conductive composite	Temperature self-controlled heater
Magnetic Function	Permanent magnet composite	Magnetic induction and magnetic memory components
	Soft magnetic composite	Magnetic control, magnetic core

收稿日期：2012-01-27；修回日期：2012-03-17
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(Table 1 continued)

Optical Function	Light transparent composite Photoluminescence composite Photochromic composite materials Photoelectric conversion composite Optical recording composite	Green house roof-panel and infrastructural constructions Fluorescent display panel Optic storage, control, switch and devices Photoconductive camera tube Optic memory devices
Thermal Function	Ablative thermal protection composite Heat adaptive composite Flame-retardant composite	Solid rocket motor nozzle, spacecraft thermal protection Semiconductor support plate Vehicle, ship, aircraft interior decoration materials
Acoustic Function	Sound-absorbing composite（in air） Sound-absorbing composite（in water） Sound functional composite	Noise barriers Muffler plate Ship sonar
Mechanical Function	Frictional resistance composite Damping composite	Bearing brake Mechanical shock absorber
Armor Function	Soft bulletproof armor Composite laminate bulletproof armor Ceramic / composite bulletproof armor	Human body armor Bulletproof helmet, military vehicle bullet-proof armor Aerospace composite armor

In the following sections, the focus will be placed on the thermal protection composites in space vehicle applications.

2 Spacecraft thermal protection system (TPS) and materials [2-4]

One of the important issues for space vehicles or orbiters is the severe environment with extreme temperature during launch and re-entry in atmosphere. For example, the spacecraft should be required to withstand temperature up to 3 000 ℃ while coming back to the Earth; while for intercontinental missiles, the temperature may reach up the range of 8 000 ℃ to 10 000 ℃, so the thermal protection is a very critical issue.

The thermal protection system (TPS) is a material system installed on the outside of the spacecraft skin, for meeting the flying aerodynamic requirements for the spacecraft and, at the same time, acting as the heat shield. The TPS covers essentially the entire outer-surface of the vehicle, and consists of seven different materials in various locations based on the required heat protection. The temperature distribution on the spacecraft surface and the locations of the TPS materials are shown in Fig. 1.

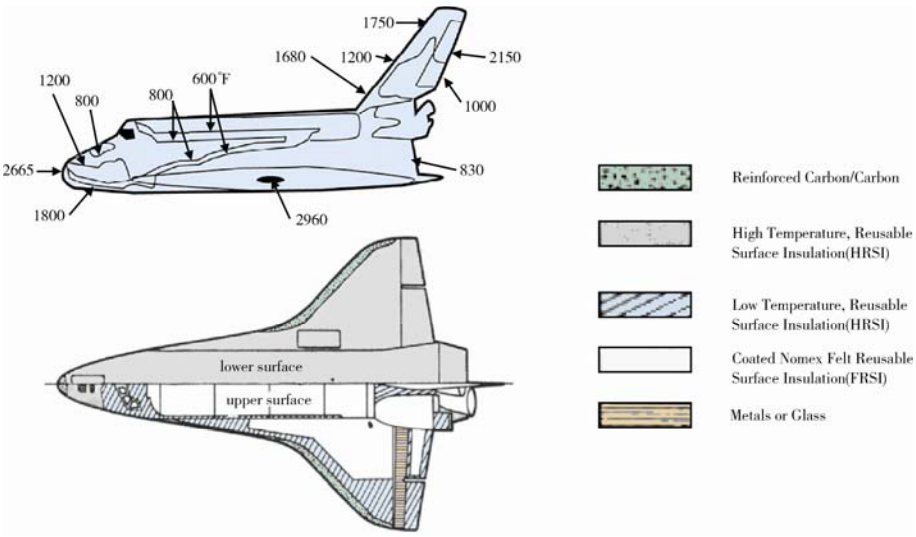

Fig. 1 Estimated surface temperature distribution and TPS materials

2.1 Reinforced carbon-carbon composite (RCC)

The fabrication of RCC begins with a rayon cloth graphitized and impregnated with a phenolic resin. This impregnated cloth is layered up as a laminate and cured in an autoclave. After being cured, the laminate is pyrolized to convert the resin to carbon, which is then impregnated with furfural alcohol in a vacuum chamber, cured and pyrolized again to convert the furfural alcohol to carbon. This process is repeated three times until the desired carbon-carbon properties are achieved.

The reinforced carbon-carbon is a light-mass and high-temperature thermal protection composite with high thermal conductivity, high melting point and high specific heat, and can be used on the wing leading edges and the nose cap, including an immediate aft area of the nose cap on the lower surface; and the immediate area around the forward orbiter/external tank structural attachment. The RCC protects the areas where temperatures would exceed 1 600 ℃ during re-entry.

The new advanced carbon-carbon (ACC) composite is available with the strength double that of the RCC, while with the oxidation mass loss only half of that of the RCC.

2.2 High-temperature reusable surface insulation (HRSI)

The HRSI is a kind of low-density, high-purity silica amorphous fiber (fibers derived from common sand, 1 ~ 2 mil thick) insulation that is made rigid by ceramic bonding. A slurry containing fibers mixed with water is frame-cast to form soft, porous blocks in which a colloidal silica binder solution is added. When it is sintered, a rigid block is produced, and then is cut into quarters, finally machined to the precise dimensions required for individual tiles with the thickness varied from 1 inch to 5 inch. The variable thickness is determined by the heat load during entry.

In fact, the HRSI is a ceramic fiber reinforced ceramic matrix composite with light mass, and is used in some areas on the upper forward fuselage, including places around the forward fuselage windows; the entire underside of the vehicle where the RCC is not used; the leading and trailing edges of the vertical stabilizer; the wing glove areas; the places adjacent to the RCC on the upper wing surface; and the upper body flap surface. The HRSI tiles protect the areas where temperatures are below 1 300 ℃. These materials have a black surface coating for absorbing emittance.

2.3 Low-temperature reusable surface insulation (LRSI)

The LRSI tiles are of the same materials and construction and have the same basic functions as the silica HRSI tiles, but they are thinner (0.2 ~ 1.4 inch) than the HRSI tiles. Thickness is determined by the heat load during entry. The LRSI tiles are manufactured with the same method as the HRSI tiles, except that the tiles are 8- by 8-inch squares and have a white optical and moisture-resistant coating 10 mil thick on the top and sides.

The LRSI are used in selected areas of a shuttle, such as the vertical tail and the upper wing. These materials protect the areas where temperatures are below 600 ℃. The materials are white in color since the shuttle would be in extremely low temperatures in orbit, and the white surface provides better thermal characteristics when the temperature is below 0 ℃.

2.4 Coated Nomex felt reusable surface insulation (FRSI)

The FRSI is made of a Nomex material, basically an aramid fiber, with thickness from 0.16 to 0.4 inch depending on the heat load during entry. It consists of sheets of 3 to 4 feet square. The FRSI is bonded directly to the orbiter by room temperature vulcanization (RTV) silicon adhesive applied at a thickness of 0.20 inch. A white-pigmented silicon elastomer coating is used to waterproof the felt and provide required thermal and optical properties. The FRSI covers nearly 50 percent of the orbiter's upper surfaces.

White blankets made of coated Nomex felt reusable surface insulation are used on the upper payload bay doors, and portions of the upper wing surface. These blankets are used in the areas where the temperature does not exceed 400 ℃.

2.5 Additional materials

These materials include glass and metal, and are used in other special areas, such as thermal glass panes for the windows; metal for the forward reaction control system fairings and elevon seal panels on the upper wing connected to elevon interface, umbilical doors, elevon cove, mid-fuselage vent doors, payload bay doors, rudder/speed brake.

The TPS materials have three key characteristics for reusable space vehicles:

1) Reusability: the ablative heat shields are commonly used for spacecraft, which would burn off during reentry and could not be reused. This TPS insulation is robust and reliable. The expendable nature is appropriate for an expendable vehicle; by contrast, the reusable shuttle requires a reusable thermal protection system.

2) Lightweight: the ablative heat shields are very heavy. The spacecraft has much more surface area than other vehicles, so a lightweight TPS is crucial.

3) Fragile: due to the very low density, TPS materials are so fragile that could be easily crushed by hand during installation

The development of TPS materials concerns with the multiple composition, the composite construction and the integration of structure and materials.

3 Ablative composites[5-7]

Ablative composites are referred to any polymer or resin matrix composites with low thermal conductivity being pyrolyzed layer-by-layer with its surface being heated, leaving a heat-resisting layer of charred material eventually broken away to expose the virgin material. Ablative composites are used on re-entry rockets and space vehicles to isolate and protect them from hyperthermal effects of the environment.

Ablative materials can be divided into three groups: subliming or melting ablators, intumescent ablators and charring ablators. Subliming ablators, such as the Teflon, carbon-carbon composites, act as heat sinks until the surface reaches the sublimation or melting temperature, taking heat out from the insulation material. Intumescent ablators form a foam-like regions exposed to heat, to improve the insulation performance. The charring ablators are basically polymer matrix composites reinforced by fibers or fabric materials, for endothermic chemical decomposition into charred materials to take place at the reaction temperature, and to produce gaseous products, so most of the heat can be taken away from the vehicle's surface. At the present, the charring ablative composites are most widely used in the space vehicle thermal protection.

The mechanism of materials ablation at high temperature is very complex, and so far is not well understood. A possible appropriate explanation for the fiber reinforced ablative composites is as follows. Initially, the heat incident to the surface is absorbed and conducted into the material substrate. The heat penetrates at a low rate, due to the very low thermal conductivity of the ablator. The surface temperature thus rises rapidly, and the thermal degradation would begin in several ways. Organic components of the composite are vaporized into numerous gaseous products in various molecular weights, often leaving behind a residual char layer. This kind of carbonized structure can result in surface recession, thus exposing the reinforcing fiber to the hot gas stream and causing fiber fusion. The molten materials cover the surface as a film or as droplets. This melt is partially vaporized, and the remainder covers the surface under the external forces of gas pressure and shear.

Based on the description above, the ablative degradation of the composite can be possibly identified in four distinct layers as shown in Fig. 2.

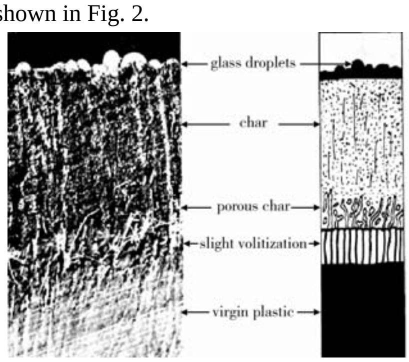

Fig. 2 Schematic diagram of the construction of ablated glass fiber composite

First, the surface material is removed by the combined action of thermal and mechanical effects. On the ablated surface is a thin film and several droplets of melted glass, formed from the reinforcing fibers. Under this surface layer is a porrous carbonized material layer reinforced by residual glass fibers. The volatile-loss layer resulted from slight loss of organic resin is adjacent to the char layer. Finally the virgin material lies beneath these damaged zones, with little or no rise in temperature because the most heat is absorbed in the aforementioned four layers.

At the early stage, the ablative composites are basically glass fiber reinforced plastics, now a variety of ablative composites have been developed with different resin matrices and reinforcing fibers.

3.1 Resin matrix

The selection of resin matrices is very important for the ablative performances of the composites. The heat resistance is the essential requirement in the selection. The current widely used matrices are silicone, polyaryl acetylene, polyimade and phenolic resins.

Silicone resins, including silicone rubbers, are organic siloxane ablative materials, which are high temperature and oxidation resistant, and are mostly used as thermal protection coatings.

Polyaryl acetylene resins are the matrices containing benzene ring and acetylene group in molecular constructions, their cured resins have very high molecular cross-linked structures and provide excellent high temperature resistance, their initial decomposition temperature is higher than 460 ℃, and the maximum decomposition temperature can reach up to 660 ℃. They are the potential candidates for the next generation of carbon-carbon composites and ablative thermal protection composites in space applications.

Polyimade (PI) resin can withstand temperature as high than 350 ℃ in long-term, and is now more and more used as the matrix for high temperature composites. Now PMR polyimade (in situ polymerization of monomer reaction) resins are the most commonly used in aerospace applications, PMR polyimade can offer a good processing ability and achieve a good impregnability to fibers.

Phenolic resins are the earliest matrix for ablative composites of low cost, easy processing and good ablative performance, and are now still widely used in thermal insulation materials for short- and middle-range solid rocket motors. Traditional phenolic resins have the shortcomings of high brittleness, large cured shrinkage and high moisture absorption, so extensive development work was carried out for their modifications, and molybdenum, boron, phenylphenol, phenolic triazine and open -loop modified phenolic resins have been developed with high thermal resistance and good ablation performance.

3.2 Reinforcement

Fibers and particles are the main elements in the reinforcement for ablative composites, where fibers can offer higher mechanical properties and heat flow erosion resistance.

There are various glass fibers, and SGFs (strength glass fibers) or HSGFs (high-silica glass fibers) are the mainly used products for reinforcement, both of which are used to make various high temperature resistant and ablative phenolic resin composite structural components for rocket and missile thermal protection.

Carbon fiber (CF) is high performance reinforcement and can be used for many types of composites including resin, metal and ceramic matrix composites, with good mechanical and thermal properties. CF reinforced composites are light in mass and high in mechanical strength, and can be used for aerospace structures integrated with some special functions, such as thermal protection, wave transmittance and wave absorption.

Other fibers for reinforcement include aromatic fibers, continuous basalt fibers and UHMWPE fibers, one relatively new fiber polybenzobisoxazole (PBO) has the elastic modulus and tensile strength almost double those of aramid fiber and with the service temperature almost 100 ℃ higher.

4 Functional gradient materials (FGMs)[8-10]

FGMs are the new type of composites developed for aerospace extreme environmental applications, characterized by spatial and continuous distributions of composition and/or microstructure of (two or more kinds of) materials in definite directions. They can be obtained by using different reinforcements with different properties, sizes and/or shapes, as shown in Fig. 3.

The following approaches are involved:

1) The use of ceramics on a surface exposed to high heat loads so as to enable a high level of heat resistivity.

2) The use of metallic materials on the other portions so as to yield high thermal conductivity and high mechanical strength.

3) The control of composition, microstructure and porosity ratio between the inner and the outer surfaces in order to adjust the different thermal expansion coefficients.

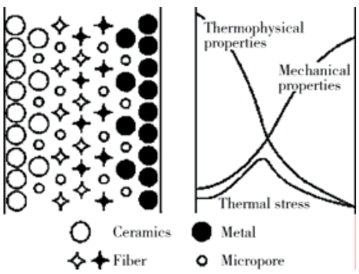

Fig. 3　Schematic diagram of FGM

As shown in Fig. 3, the FGMs have a continuous (or gradual) distribution in material composition, microstructure and the physical parameters. For applications in environments with very large temperature differences, on the high temperature side, the heat-resistant ceramic materials are used, while on the low temperature side, high strength and thermal conductive metals are used. From ceramic to metal, the heat resistance is gradually decreased, while the mechanical strength is increased, the thermal stresses on both sides are very small, and reach the maximum values in the middle layer, and the thermal stress relaxation will be functionalized.

Significant progresses have been made for FGMs since its emergence on the 1980s, and at the present, the commonly used FGMs include SiC/C, Ni/A1203, NiCrAlY/SiC, Al/SiC, etc. FGMs can be used in spacecraft hot structures such as turbine engine blade, rocket nose cap, rocket thrust chamber, and spacecraft wing lead edge.

As an innovative composite, further fundamental researches are being carried on in the following aspects:

1) FGM design. A design expert system should be developed to carry on numerical simulations in which the structure types are determined and the boundary conditions are specified. With an assumed mixture ratio of selected materials and their distribution, the temperature and thermal stress distribution within the FGM are calculated using the material properties estimated from the microstructures of the FGM. Various possible material mixture ratios and distributions are considered to obtain the optimized combination of selected materials.

2) FGM processing. The major goal is to develop new processing technologies for synthesizing and integrating large size and complex shape structures with a more accurate gradient composition distribution. The current processing technologies include physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods, the powder metallurgical method, the plasma spray coating method and the self-propagating high temperature synthesis method.

3) FGM evaluation. The adequate performance evaluation system including testing procedures, database and standardization is very important, which should be concentrated on the thermal behaviors of the FGM including the thermal stress relaxation, the thermal fatigue, the thermal shock and the thermal insulation.

5 Conclusions

The new generation of space vehicles are developed in the direction for hypersonic, manoeuvrable and reusable flight, so that the novel functional composite materials are increasingly needed in the place of the traditional thermal composites. In general, the development of functional composites for space applications features high performance, light mass, multiple functions and low-cost. New materials and processing technologies are continuously developed.

5.1 High performance and light mass

New generation space vehicles require the development of some key materials with high performances and special functions, for example, to increase the landing accuracy of the orbiter, the manoeuvring, breakthrough and all-weather capacities, the thermal protection layers for re-entry orbiter are required for uniform and symmetric ablation profiles, and also the minimized ablation mass. For the solid rocket motor nozzle throat, the ablation mass should be as small as possible, and the ablated surface should be regular; besides, stringent requirements are necessary for the insulation capacity and density of thermal functional materials for long-term flight.

5.2 Multiple functions

Most of the hot structures are required to provide other special functions in addition to the thermal function, such as the structural and functional integration, the thermal protection with wave transmitting/absorption and the stealth function, and at the same time, the ablative and insulation functions, etc.

5.3 Low-cost

The ratio of performance to price is one of the most concerned issues in advanced composites. The low-cost includes considerations in the design for manufacture (DFM), the alternative material selection, the low-cost processing technologies with high production efficiency and low production cost.

5.4 Innovative technologies [11-12]

Nano materials, essentially carbon nanotubes (CNTs), offer extraordinary stiffness and specific tensile strength and can greatly increase the strength and stiffness of a polymer matrix with minimal increases in weight. It can also increase the ability of a composite to resist thermal attack and to achieve flame retardant.

There are a number of technical challenges that must be tackled before carbon nanotube reinforced-polymer composites can become commercially available, such as large aspect ratio, interfacial stress transfer, good dispersion, and alignment.

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航天功能复合材料发展现状及趋势

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摘要：文章综述了航天功能复合材料的发展现状及趋势，内容包括各种类型的功能复合材料及主要应用领域。对当前用于航天领域的热防护功能复合材料分别作了重点介绍，包括航天器热防护系统及材料、抗烧蚀热防护复合材料、梯度功能复合材料以及它们的组成、作用机理和主要应用。最后探讨得出功能复合材料的发展趋势是高性能化、多功能化和低成本化。

关键词：先进功能复合材料；航空航天应用；热防护；综述