Materials

Low-Density Resin-Based Ablative Heat Protection Materials

Johnson M. Willard*
Nova Materials, Inc., San Francisco, CA 94108, USA
*: All correspondence should be sent to: Dr. Johnson M. Willard.
Author's Contact: Johnson M. Willard, PhD, E-mail: jmwillard@novamat.com
DOI: https://doi.org/10.15354/si.22.re063
Funding: No funding source declared.
COI: The author declares no competing interest.

The severe aerodynamic heating that occurs when a spacecraft reenters the atmosphere takes place. The material used for thermal protection is an essential part of the system used for thermal protection. A number of chemical and physical transformations take place in the ablation heat-resistant material that is based on resin. This material is an organic polymer. We herein briefly review the status quo of low-density resin-based ablative heat protection materials.

Keywords: Spacecraft; Aero-Thermal Environment; Heat-Resistant Materials; Thermal Protection; Multifunction

Science Insights, 2022 May 31; Vol. 40, No. 6, pp.541-544.

WHEN a spacecraft reenters the atmosphere, intense aerodynamic heating ensues. The thermal protection system is one of the major subsystems that must be relied on to ensure the normal operation of the aircraft's electronic components and manned spaces, and thermal protection material is an integral component of the thermal protection system (1). The thermal environment becomes more severe with increasing reentry velocity (2). When the pneumatic heating time exceeds 1,000 seconds, the heating quantity increases significantly, a large area is exposed to the high temperature (1,000 ℃) of a long-term aerobic environment, and the instantaneous temperature of the essential components can reach more than 2,000 ℃.

Since the 1950s, spacecraft thermal protection material systems and thermal protection procedures have undergone continual development, particularly ultra-lightweight, reusable thermal protection materials, such as ceramic tiles and TUFROC (3). It has been effectively implemented and has garnered considerable interest from scientists and engineers. However, in general, these materials have poor reliability, a high price, a difficult manufacturing process, and high maintenance expenses, which restricts their widespread use in aeronautical vehicles (4). Resin-based ablation heat-resistant material is based on organic polymer and undergoes a series of chemical and physical changes, sacrificing the quality of the material in order to remove a great deal of aerodynamic heat and therefore achieve its intended purpose (5). Due to its high dependability, excellent cost performance, and simple assembly procedure, it is still regarded as the most effective, reliable, mature, and cost-efficient way of thermal protection.

Low-Density Resin-Based Ablative Heat Protection Material

Honeycomb Reinforced Low Density Heat Protection Material

H88 and H96 materials are supported by a glass fiber reinforced plastic honeycomb lattice, phenyl silicone rubber as the resin matrix, doped with quartz short fibers, phenolic microspheres, glass microspheres, and other lightweight functional fillers by physical blending, and rapidly filled by an integral molding process into the fiberglass honeycomb lattice (6). The inclusion of lightweight functional fillers is primarily employed to decrease material density and thermal conductivity, while ensuring the surface's resistance to airflow erosion (7). FG4 and FG5 materials with densities of approximately 0.4 g/cm3 and 0.5 g/cm3 were developed, and the thermal conductivity at room temperature was less than or equal to 0.1 W/ (m•K) for the low-to-medium heat flow area on the leeward side of the reflector side wall (8). In the high heat flow region of the heat-proof outsole of the returner, 0.5 g/cm3 and 0.7 g/cm3 HC5 and FG7 materials with a thermal conductivity of 0.10-0.12 W/(m•K) at room temperature were produced (9). This is to improve the ablation performance and shear resistance of thermal protection materials at high stagnation points.

Thermal Insulation Integrated Low-Density Resin-Based Thermal Insulation Material

In the 1990s, aerospace powers dominated by the United States developed successively new models to meet the heat protection and heat insulation requirements of advanced spacecraft such as those used for deep space exploration and the space shuttle, and to further compress the mass ratio of the heat protection system in the overall system (10). Typical examples of thermal insulation integrated ultra-low density ablation thermal protection materials include PhenCarb, BLA, SCRAM, PICA, and SIRCA. This category of materials is distinguished by its ultra-low density (0.35 g/cm3), ultra-low thermal conductivity, and compatibility with thermal and thermal insulation (11).

The SPQ family of medium and low density quartz/phenolic, glass/phenolic system heat-resistant materials were created using the oblique winding molding method. The primary characteristic of SPQ material is that a large amount of lightweight functional fillers, such as phenolic microspheres, glass microspheres, and ceramic powders, are added to the phenolic resin matrix, and a two-dimensional fabric woven from quartz fibers and functional fibers is used as the reinforcing phase to produce lightweight functional fillers (12). By modifying the composition of the reinforcement and resin matrix, hybrid prepreg can be used to produce SPQ series materials that meet various heat protection criteria (13). The incorporation of hollow spheres and micropores can dramatically reduce the heat conductivity and density of the material, respectively. SPQ series materials are inherited materials that have been enhanced by the conventional oblique winding molding procedure (14). Compared to traditional dense glass/phenolic, quartz/phenolic heat-resistant composite materials, the density of SPQ materials can be reduced by a maximum of 43%, and the room-temperature heat conductivity is reduced to approximately 50% of that of traditional heat-resistant materials (15). SPQ materials have been successfully applied to the thermal protection of key components of lunar orbital returners, weapons, and equipment.

To address the requirements of new aerospace vehicles for weight reduction, heat protection, heat insulation, and radar stealth, a lightweight heat protection/heat insulation/stealth integrated material (HRC) was created. To meet the thermal load requirements of important thermal protection components of spacecraft at high temperature, we must create a heat-resistant/heat-insulating/load-bearing integrated composite material (HIS) with a density of 1.2 g/cm3 (16). A multifunctional integrated material of heat-resistant/heat-insulation/flame retardant has been invented to address the phenomenon of open flame burning when the heat-proof skirt material of the launch vehicle engine is ignited (17). This material effectively solves the problem of the open flame of the heat-proof skirt when the rocket engine is ignited.

With the continual development of advanced aerospace vehicles and flight control technology, the aircraft's ballistic procedures and flight thermal environment are growing more diversified and complicated, and the functional requirements for heat-resistant materials are becoming more demanding. Thermal technology is an indispensable technical instrument for simultaneously solving the complex thermal protection system of future spacecraft.

Research Prospect of Low-Density Resin-Based Ablative Heat-Resistant Materials

Multifunctional Compatibility and Integration

The heat-resistant material is the outermost component of the re-entry spacecraft and serves as a barrier against the aero-thermal environment (18). In addition to meeting the requirements for aerodynamics and heat resistance, it must also possess thermal insulation, anti-scour, thermal bearing, and aerodynamic dimensions. Due to the increasingly severe flight thermal environment of spacecraft, the continuous extension of heating time, and the stringent quality requirements of thermal protection systems, the development trend of low-density resin-based ablative heat-resistant materials must be to achieve thermal protection on the basis of lightness (19). Compatibility and integration of multiple functions, including thermal insulation, aerodynamic shape, thermal bearing, stealth, and flame resistance, are crucial for the novel materials. The future development trend of low-density resin-based ablative thermal composite materials is to reduce the costs of thermal protection system design, assembly, and maintenance.

Synergy of Multiple Thermal Protection Mechanisms

Ablation and heat protection materials endure a series of complex physical and chemical responses in the aerodynamic thermal environment, are closely connected to the thermal environment, and undergo an unstable mass transfer and heat transfer process (20). The investigation of thermal mechanism has traditionally been regarded as the most difficult field of inquiry. During the ablation process of the material, a significant amount of aerodynamic heat heats the surface of the material via convection and radiation, followed by a complex chemical reaction in which the resin matrix decomposes and absorbs a significant amount of incoming heat, and the pyrolysis product forms a porous carbonized layer. It is of great importance to clarify the mechanism of various thermal protection mechanisms in the resin-based ablation thermal protection material during the entire thermal protection process and the proportion in the total thermal effect, reveal the mutual coupling between various thermal protection mechanisms, and demonstrate unstable combustion (21). The process of heat and mass transfer within the material body during the ablation process, gaining an understanding of the relationship between the microstructure and performance of the material, and contributing to the realization of synergy and matching between the heat protection, heat insulation, and other functions of the low-density resin-based ablation heat protection material system. It has very essential scientific guiding value for the structural design, development, preparation and engineering application of new resin-based LAC materials.■

References

1. Le VT, Ha NS, Goo NS. Advanced sandwich structures for thermal protection systems in hypersonic vehicles: A review. Compos B Eng 2021; 226:109301. DOI: https://doi.org/10.1016/j.compositesb.2021.109301
2. Miao W, Li Q, Li J, Zhou J, Cheng X. Thermal environment and aeroheating mechanism of protuberances on mars entry capsule. Space Sci Technol 2021; 2021:9754068, DOI: https://doi.org/10.34133/2021/9754068
3. Pirolini A. Materials Used in Space Shuttle Thermal Protection Systems. AZO Materials 2014; Last access: May 20, 2022. Available at: https://www.azom.com/article.aspx?ArticleID=11443
4. Thomas DS, Gilbert SW. Costs and cost effectiveness of additive manufacturing: A literature review and discussion. National Institute of Standards and Technology (NIST) Special Publication 1176, 2014; DOI: http://dx.doi.org/10.6028/NIST.SP.1176
5. Pulci G, Tirillò J, Marra F, Fossati F, Bartuli C, Valente T. Carbon-phenolic ablative materials for re-entry space vehicles: Manufacturing and properties. Compos A Appl Sci Manuf 2010; 41:1483-1490. DOI: https://doi.org/10.1016/j.compositesa.2010.06.010
6. Li Z, Ma J. Experimental study on mechanical properties of the sandwich composite structure reinforced by basalt fiber and Nomex honeycomb. Materials 2020; 13(8):1870. DOI: https://doi.org/10.3390/ma13081870
7. Hanif A, Lu Z, Cheng Y. Diao S, Li Z. Effects of Different Lightweight Functional Fillers for Use in Cementitious Composites. Int J Concr Struct Mater 2017; 11:99-113. DOI: https://doi.org/10.1007/s40069-016-0184-1
8. Debnath T, Debnath B, Lake RK. Thermal conductivity of the quasi-one-dimensional materials TaSe3 and ZrTe3. Phys Rev Materials 2021; 5:034010. DOI: https://doi.org/10.1103/PhysRevMaterials.5.034010
9. O'Regan M, Preto P, Stranne C, Jakobsson M, Koshurnikov A. Surface heat flow measurements from the East Siberian continental slope and southern Lomonosov Ridge, Arctic Ocean. Geochem Geophys Geosyst 2016; 17:1608-1622, DOI: https://doi.org/10.1002/2016GC006284
10. Wang J, Li Y, Liu X, Shen C, Zhang H, Xiong K. Recent active thermal management technologies for the development of energy-optimized aerospace vehicles in China.Chinese Journal of Aeronautics 2021; 34(2):1-27. DOI: https://doi.org/10.1016/j.cja.2020.06.021
11. Dutta M, Matteppanavar S, Prasad MVD, Pandey J, Warankar A, Mandal P, Soni A, Waghmare UV, Biswas K. Ultralow thermal conductivity in chain-like TlSe Due to inherent Tl+ rattling. J Am Cheml Soc 2019; 141(51):20293-20299. DOI: https://doi.org/10.1021/jacs.9b10551
12. Riccucci G, Pezzana L, Lantean S, Tori A, Spriano S, Sangermano M. Investigation of the thermal conductivity of silicon-base composites: The effect of filler materials and characteristic on thermo-mechanical response of silicon composite. Appl Sci 2021; 11:5663. DOI: https://doi.org/10.3390/app11125663
13. Maurizio N, Marco R, Luigi T, Debora P. High temperature composites from renewable resources: A perspective on current technological challenges for the manufacturing of non-oil based high char yield matrices and carbon fibers. Front Mater 2022; 9:805131. DOI: https://doi.org/10.3389/fmats.2022.805131
14. Miao Y, Geng Y, Li X, Liu X. Tension system design based on heated-mandrel winding process. J Comp Mater 2022; 56(7):1091-1105. DOI: https://doi.org/10.1177/00219983211069200
15. Li H, Wang N, Han X, Fan B, Feng Z, Guo AS. Simulation of thermal behavior of glass fiber/phenolic composites exposed to heat flux on one side. Materials (Basel) 2020; 13(2):421. DOI: https://doi.org/10.3390/ma13020421
16. Dorsey J, Chen R, Poteet C, Wurster K. Metallic thermal protection system requirements, environments, and integrated concepts. J Spacecraft Rocket 2004; 41:162-172. DOI: https://doi.org/10.2514/1.9173
17. Sun C, Xia R, Shi H, Yao H, Liu X, Hou J, Huang F, Yip H-L, Cao Y. Heat-Insulating Multifunctional Semitransparent Polymer Solar Cells. Joule 2018; 2(9):1816-1826.DOI: https://doi.org/10.1016/j.joule.2018.06.006
18. Fahrenholtz W, Hilmas G. Oxidation of ultra-high temperature transition metal diboride ceramics. Int Mater Rev 2012; 57:61-72. DOI: https://doi.org/10.1179/1743280411Y.0000000012
19. Delfini A, Albano M, Vricella A, Santoni F, Rubini G, Pastore R, Marchetti M. Advanced radar absorbing ceramic-based materials for multifunctional applications in space environment. Materials (Basel) 2018;

11(9):1730. DOI: https://doi.org/10.3390/ma11091730

20. Ungar EW. Ablation Thermal Protection Systems: Suitability of ablation systems to thermal protection depends on complex physical and chemical processes. Science 1967; 158(3802):740-744. DOI: https://doi.org/10.1126/science.158.3802.740
21. Bahramian A, Kokabi M. Ablation mechanism of polymer layered silicate nanocomposite heat shield. J Hazard Mater 2008; 166:445-454. DOI: https://doi.org/10.1016/j.jhazmat.2008.11.061

Received: March 09, 2022 | Revised: March 27, 2022 | Accepted: April 03, 2022