



Letter

A direct chemical vapor infiltration route for a carbon nanotube/silicon carbide thermal protection system



A B S T R A C T

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Sandwich-structured carbon nanotube/silicon carbide (CNT/SiC) sponges were fabricated by direct chemical vapor infiltration (CVI) of SiC matrix into the inner network of CNT sponges without altering the original sponge morphology. The thermal conductivity of the sandwich-structured material from 25 °C to 1200 °C was established in the range of 2.3–4.3 W/mK range. The values were much lower than the pure SiC, which indicates that the material can efficiently dissipate heat along the SiC coating. Based on the design of the sandwich structure produced by direct CVI process, large fiber preforms combined with one-dimensional nano-materials that aid the reduction of surface pore size will be an inspired idea for the design of sandwich-structured large fiber composites.

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1. Introduction

Extensive investigations have revealed that thermal protection systems (TPS) are key to the successful development of a wide selection of hypersonic vehicles ranging from ballistic reentry to hypersonic cruise vehicles [1]. As TPS protect underlying structures within acceptable temperature limits and provide sufficient structural strength and stiffness for retaining of the aerodynamic shape, it should provide high temperature tolerance and low weight. To meet the primer requirement and endure severe aerodynamic heating, TPS must be constructed of materials with high melting points and high oxidation resistance [2]. At present, silicon carbide ceramic matrix composites (SiC CMCs) are among the most relevant materials; they show great TPS potential below 1600 °C due to their thermal stability at high temperatures, low density, high stiffness, good strength, high toughness, erosion resistance and self-passivating behavior in oxidizing environments [3]. Above 1600 °C, ZrB₂-based ultra-high temperature ceramics have attracted much attention owing to their unique combination of high melting points, thermal shock resistance as well as excellent mechanical and chemical stability. Such materials are becoming promising candidates in applications targeted for extremely severe environments, including sharp leading edges, nose cones and other TPS for reusable atmosphere re-entry hypersonic flights [4].

TPS must also be lightweight in order to increase the thrust-to-weight ratio as well as to improve the effective loading weight. Efforts are on to develop what is termed as integral TPS, sandwich structures not only thermally protect the structure, but also withstand high loads [2]. At present, a lot of sandwich structures, such as corrugated panels, lattices, and honeycombs, have been widely investigated. For example, ZrB₂/SiC/graphite corrugated panel [4], low density C/SiC pyramidal core lattice sandwich panel [5], and SiC-based laminate containing porous layers [6] have been

proposed for potential TPS applications.

The present study introduces the design of a novel sandwich structure produced by SiC-coated carbon nanotube/SiC (SiC-CNT/SiC) sponges. Therein, chemical vapor infiltration (CVI) is employed for the infiltration of SiC (we term it SiC matrix) into the open network of CNT sponges, which are bulk cotton-like CNT structures consisting of interconnected self-assembled branches of CNTs. The resultant material is termed CNT/SiC sponges. Under prolonged CVI durations, dense SiC matrix layer, which was termed SiC coating, can form on the outer surface of the CNT/SiC sponges. The thermal conductivity and diffusivity of the materials was measured and compared to the pure SiC.

2. Experimental

Bulk, cotton-like CNT sponges fabricated by floating catalyst chemical vapor deposition were supplied by Suzhou Institute of Nano-Tech and Nano-Bionics, (China). The starting CNT sponges were cut by surgical scalpel into rectangular blocks of dimensions of 60 × 60 × (3–5) mm³, then the four sides were clamped with a graphite clip and inserted into the CVI furnace for SiC matrix infiltration. The CVI process utilized methyltrichlorosilane (MTS, CH₃SiCl₃) as precursor gas, hydrogen (H₂) as carrier gas, and argon (Ar) as diluting gas. The H₂: MTS molar ratio, temperature, and pressure were 10, 1015 °C, and 2 kPa, respectively, both of the flow rates of H₂ and Ar were 3.0 L/min, and the single-step CVI duration was 80 h.

Specimen density, ρ , and thermal conductivity, K , were calculated as $\rho = m/V$ and $K = D\rho C_p$, respectively, where D is the thermal diffusivity and C_p is the specific heat. The latter parameters were measured directly by laser flash apparatus (LFA427, NETZSCH Company, Germany). Five specimens and three different positions for every specimen were tested for statistically accurate calculation.

The microstructure of the materials was observed by scanning electron microscopy (SEM) (Hitachi S-4800, Tokyo, Japan).

3. Results and discussion

As shown in the SEM micrograph of Fig. 1, the starting nanotube sponges consisted of CNTs with rather high aspect ratios and high degree of entanglement; the tubes were self-assembled into a porous, interconnected, isotropic, three-dimensional (3D) network structure. The growth process of the CNT sponges can be regarded as a consecutive stacking and interpenetration of many CNT “piles” into centimeter thickness. Individual CNTs in the sponges had external diameters in the range of 30–50 nm and lengths of tens to hundreds of micrometers. The porosity of the sponges was approximately 99%, and their bulk density was about 4–8 mg/cm³. Since the CVI process is strongly dependent on gas diffusion mechanisms, the CNT sponges’ particular morphology conditions are anticipated highly dependent on gas flow throughout the material volume allowing the chemical reaction of gaseous species flowing by diffusion through the pores. On the other hand, the small pore sizes achieved by the CNT morphology render infiltration uniformity more challenging than conventional CVI of micron-scale fiber preforms [7]. Here, SiC matrix deposition is expected to initially concentrate around the external surfaces of CNT sponges hence filling the surface porosity which will obstruct further infiltration and leave excess void space inside the sponges. After the infiltration, as-fabricated plates were polished using 800[#] grit emery paper for removing the SiC coating and polished into thin plates of 3 mm thickness gently. Then the plates were cut into cylindrical specimens with dimensions of $\varnothing 12.7 \text{ mm} \times 3 \text{ mm}$ for thermal property tests. Some specimens were further infiltrated with SiC matrix for additional 2, 4 and 6 cycles, respectively; these specimens were termed SiC-CNT/SiC sponges.

Fig. 2 demonstrates the unique microstructure of the fractured section of SiC-CNT/SiC sponges after one CVI cycle. Two neighboring parts can be seen in the cross section, namely the SiC coating and the porous CNT/SiC sponges. In the preliminary stage, MTS gas could easily penetrate and deposit SiC matrix inside the porous network of CNT sponges, moreover, the infiltration speed decreased compared to that at the surface. With time, a dense SiC coating is formed on the outer surface which blocks further SiC infiltration into the material. Fig. 3 shows the higher-magnification micrographs of the CNT/SiC sponges, it was found that individual CNTs were coated with SiC matrix. In addition, CNTs can be observed to pull out of the matrix; the relevant pullout length is considerable, which signifies that the rather high aspect ratio in the original CNT sponges did not deteriorate after the CVI process.

After one CVI cycle, the SiC coating was removed by polishing

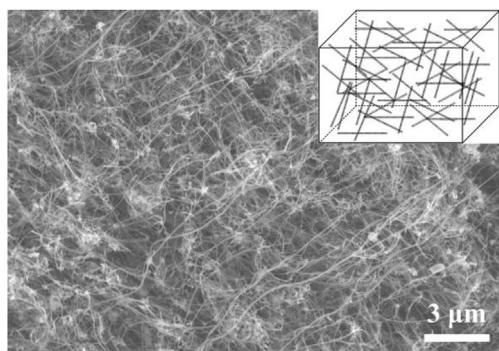


Fig. 1. SEM micrograph of the CNT sponges and illustration of 3D framework in the CNT sponges.

into plates of 3 mm thickness, and it could be visualized that pores would be observable on the specimen surface. Following additional CVI cycles, it is believed that the structure of the sponges is limited to the increasing of SiC coating thickness. The density of CNT/SiC sponges was $0.99 \pm 0.09 \text{ g/cm}^3$, after an additional 2, 4, and 6 CVI cycles, the density increased to 1.28 ± 0.02 , 1.49 ± 0.01 , and $1.56 \pm 0.01 \text{ g/cm}^3$, and the SiC coating thickness of SiC-CNT/SiC sponges was 143 ± 10 , 315 ± 9 , and $360 \pm 8 \text{ }\mu\text{m}$, respectively.

Fig. 4a shows the variation of the thermal diffusivity and conductivity of CNT/SiC sponges and SiC-CNT/SiC sponges in the range of 25 °C to 1200 °C. It is observed that the thermal diffusivity of all four specimens decreases with temperature in a similar trend. Specifically, for temperatures of 25, 200, 400, 600, 800, 1000, and 1200 °C, average thermal diffusivity values of 3.32, 2.44, 2.07, 1.87, 1.73, 1.65, and 1.52 mm²/s were established for the CNT/SiC sponges, respectively. On the other hand, it is found that the thermal diffusivity decreases with SiC coating thickness in all temperatures. This indicates that, the more SiC is infiltrated on the CNT/SiC sponge surface, the lower the thermal diffusivity. For a density of $1.56 \pm 0.01 \text{ g/cm}^3$, the corresponding average values are 2.77, 2.10, 1.77, 1.62, 1.51, 1.44, and 1.38 mm²/s, respectively. At temperatures of 25 and 200 °C, thermal conductivity of the SiC-CNT/SiC sponges under different densities is higher than that of CNT/SiC sponges, reaching 3.03 to 3.47 W/mK. As the temperature is higher than 400 °C, the thermal conductivity curves of the three SiC-CNT/SiC sponges’ specimens exhibit similar trend; the specific values for thermal conductivity ranged within 3.0–4.3 W/mK for specimens with densities of 1.28 ± 0.02 and $1.49 \pm 0.01 \text{ g/cm}^3$. These conductivities were higher than that of uncoated CNT/SiC sponges, however, for a density of $1.56 \pm 0.01 \text{ g/cm}^3$, the thermal conductivity was lower, in the range of 2.3–2.9 W/mK. Based on the thermal conductivity values, it can be understood that a threshold limit of SiC coating thickness exists for SiC-CNT/SiC sponges. Below the threshold limit, thermal conductivity is higher than SiC/CNT sponges, and above the threshold limit, thermal conductivity is lower than SiC/CNT sponges. According to the above analyses, it can be concluded that the threshold limit of SiC coating thickness is $315 \pm 9 \text{ }\mu\text{m}$. Beyond that, the relative amount of SiC matrix in the material increases with SiC coating thickness, and as it is enough high, the variation trend of the thermal conductivity of SiC-SiC/CNT sponges is similar to that of the SiC. In this study, for the density of $1.56 \pm 0.01 \text{ g/cm}^3$, the thermal conductivity at 200 °C is the highest, above 200 °C, the thermal conductivity decreases with the temperature, which is similar to the variation trend of the SiC [8]. On the other hand, an important observation is that there is a sudden drop in thermal conductivity for all the specimens at 1200 °C. In fact, from the point of thermodynamics, the CVI process is far from equilibrium state, which will lead to the internal stress exists in the SiC grain [9]. As the measured temperature was more than the preparation temperature, i.e. 1200 °C, the internal stress will be released, meanwhile, some SiO(g) were formed by the active oxidation of SiC with residual oxygen [10]. These will result in a lot of defects in the composites [11] and increase the phonon scattering, therefore, the thermal conductivity of all the specimens have a sudden drop at 1200 °C. Fig. 4b conceptually illustrates the heat transfer pattern in SiC-CNT/SiC sponges. In the range of 25–1200 °C, the thermal diffusivity of pure SiC decreases from 49 mm²/s to 8 mm²/s with the increase of temperature [12], and the thermal conductivity is 80–480 W/mK [8]. Therein, due to the much lower thermal conductivity of the SiC-CNT/SiC sponges compared to the pure SiC, heat will be conducted quickly along the SiC coating.

Such sandwich structure meets the design methodology of the TPS, however it is also crucial that the sandwich layers serve as robust load-bearing structures. In this context, SiC-CNT/SiC sponges

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