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Microstructures and mechanical properties of three-dimensional ceramic filler modified carbon/carbon composites

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Abstract

A three-dimensional needled carbon fiber integrated felt was used as the preform for SiC or B_4C modified carbon/carbon (C/C) composite: C/C–B_4C or C/C–SiC which was prepared through unidirectional pressure slurry infiltration-filtration followed by chemical vapor infiltration. There were four kinds of interface microstructure modes between ceramic filler particles and pyrolytic carbon (PyC) matrix: enwrapping, encircling, embedding and infilling. For C/C–B_4C, enwrapping, encircling and embedding were the main modes. For C/C–SiC, embedding was the main one. The addition of ceramic filler complicated some fiber/matrix interfaces, forming composite interface layers and dual interface layers. There were three kinds of characteristic fiber/matrix interfaces: $(fiber/filler/PyC)_n$/PyC, fiber/(filler/PyC)/PyC, fiber/filler/PyC. The flexure strength of C/C was 98 MPa, whereas those of C/C–B_4C and C/C–SiC were 200 and 140 MPa, respectively. The addition of ceramic filler not only increased the bonding strength of some fiber/matrix interface, but also toughened the PyC matrix.

Keywords: B. Composites; B. Fibers; B. Interfaces; C. Mechanical properties

1. Introduction

For brake materials, not only excellent tribological properties and chemical stability are required, but also good mechanical properties are necessary. A sufficient strength and damage tolerance is of great importance due to the safety sensitiveness of the brake components [1,2]. Low strength and fracture toughness will cause material damage and even catastrophic failure during the braking process. Three-dimensional (3D) needled carbon/carbon (C/C) composites introduce fiber bundles perpendicular to the lamina direction which improves the bonding strength and thermal conductivity between laminates. For C/C brakes, the extremely low friction coefficient in wet and/or corrosive environments represents an obstacle for braking applications [3]; the lower strength of C/C composites is an additional shortcoming having a negative impact on their use.

In order to break the limitations of C/C composites, it is necessary to modify the matrix by introducing some fillers or reinforcements. Park et al. [4,5] prepared C/C composite laminates with $MoSi_2$ filler, the bulk density, graphitization degree and mechanical properties being effectively improved. Gadow et al. [6,7] introduced granular ceramic or ceramic whiskers and slices into multilayer carbon/silicon carbide (C/SiC) composites to reinforce and toughen the matrix. Odeshi et al. [8] prepared two-dimensional (2D) plain weave C fiber reinforced C–SiC dual matrix composites by phenolic resin infiltration-pyrolysis followed by polysilane infiltration-pyrolysis. Their study showed the flexural and visco-elastic properties of the composite were dominated by the strength of the fiber/matrix interface rather than by the strength or modulus of fibers. Li et al. [9] introduced zirconium carbide (ZrC) into 2D C/SiC composites by vacuum infiltration with

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ZrC slurry, higher strength being obtained. Yin et al. [10] improved the mechanical properties of 3D needled C/C composites by TiC slurry infiltration into the porous C/C composite followed by liquid silicon infiltration (LSI) to in-situ synthesize Ti_3SiC_2-SiC matrix in the C matrix. We previously reported on a 3D needled C/SiC composite via graphite modifying SiC matrix, introducing graphite filler having greatly improved the mechanical property [11]. However, as far as we know, few studies on the mechanical properties of 3D needled C/C composites modified by ceramic fillers are reported.

In this study, ceramic filler was introduced to modify C matrix, and the hybrid composites with C matrix reinforced by 3D needled C fibers and ceramic filler particles were prepared. Both SiC and boron carbide (B_4C) have high strength as well as elastic modulus and good chemical inertness. Additionally, B_4C has high specific heat, which can reduce the temperature rise in the braking process. SiC or B_4C filler was introduced into a 3D needled C fiber integrated felt by a new process, unidirectional pressure slurry infiltration-filtration (UPSIF), which was followed by chemical vapor infiltration (CVI) to obtain pyrolytic carbon (PyC) matrix. This new process has an advantage over LSI process in avoiding C fibers damage by molten Si and avoiding the formation of residual Si. The characteristic interfaces in ceramic filler modified C/C composites were revealed. The mechanical behavior between ceramic modified C/C and unmodified C/C composites were compared. The toughening mechanism of ceramic fillers on 3D needled C/C composites was analyzed.

2. Experimental

2.1. Samples preparation

The 3D needled integrated felt with a density of 0.55 g/cm^3 and fiber content of 30 vol% which was described previously in detail [12] was used as the preform. The C fiber was polyacrilonitrile-based C fiber (T 700, 12 K tow, Toray, Japan). The ceramic constituent was introduced into the fiber preform by UPSIF, which was followed by CVI to prepare ceramic filler modified C/C composites.

The fiber preform (ϕ 100 mm × 15 mm) was placed in a unidirectional pressure infiltration-filtration device (Northwestern Polytechnical University, Xi'an, PR China). The bottom side of the preform clung to a millipore membrane. The fiber preform was infiltrated with the slurry containing SiC or B_4C filler powder in water medium under an inert gas pressure-driving from top to bottom. SiC and B_4C filler were 1.0 and 1.5 μm in average particle diameter respectively. The slurry was separated by the millipore membrane at the bottom of the fiber preform. The fiber preform itself is a kind of deep bed filtration medium. Most of the filler particles were retained within the fiber preform and the surface of the millipore membrane. Water and a small quantity of filler particles flowed out. The infiltration pressure and time were 0.6–1.0 MPa and 10–20 min, respectively. The volume fraction of particles in the slurry was 8–12%. All samples were performed only a one-shot infiltration-filtration process, taken out from the device and dried, and then the preform containing SiC or B_4C fillers was obtained.

The CVI process was employed to transform the preform containing the ceramic filler into the hybrid composite with C matrix reinforced by 3D needled C fibers and ceramic fillers. The temperature and time for CVI were 800–1000 °C and 300–400 h, respectively. Propylene was used as a precursor and argon as a carrier as well as diluting gas. The composites prepared by the above method were named as C/C–SiC and C/C–B_4C respectively according to the filler types.

The unmodified C/C composite using the same 3D needled integrated felt as the preform was prepared for comparison. The temperature and time for CVI process to densify the fiber preform were about 800–1000 °C and 400–700 h. Propylene was used as a precursor and argon as a carrier as well as diluting gas.

2.2. Mechanical property testing

The mechanical property of the ceramic modified and unmodified C/C composites was studied using the three-point flexural strength test (SANS CMT 4304, Sans Materials Testing Co., Shenzhen, China). The support span was 30 mm and the cross-head speed 0.5 mm/min. The load direction was perpendicular to the layers of the C felt. Five samples were tested to obtain the average strength. The sample size was 40 × 5 × 3.5 mm^3.

2.3. Microstructure characterization

The open porosities and bulk densities of samples were measured by Archimedes' method. The microstructures and fracture surfaces were examined by scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDX, S-4200, Hitachi, Japan). The mass contents of C and SiC in C/C–SiC were determined according to the gravimetric analysis [13]. The content of C was measured by burning it off at 700 °C for 20 h in air, and the SiC-content could be calculated.

3. Results and discussion

3.1. Microstructure characterization

3.1.1. Filler contents and densities

The densities of ceramic filler modified C/C composites were slightly lower than those of the unmodified C/C composite, while the open porosities were higher (Table 1), which was attributed to the shorter densification time. Their densities were greatly reduced compared with those of C/SiC composites (generally higher than 2.00 g/cm^3), which is beneficial for reducing weight of brake materials.

The mass content of SiC filler in C/C–SiC was measured by the gravimetric analysis. The calculation values of volume content v_f and mass content w_f of the ceramic filler in a modified C/C composite were based on the formulas