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Comparison of thermal and ablation behaviors of C/SiC composites and C/ZrB_2–SiC composites

Sufang Tang, Jingyi Deng *, Shijun Wang, Wenchuan Liu

Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road 72, Shenyang 110016, China

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ABSTRACT

A comparison was presented of the thermal and ablation behaviors of two carbon fiber reinforced ceramic–matrix composites (one with a SiC matrix and the other with a ZrB_2–SiC matrix). The C/SiC composite possessed a lower thermal conductivity (TC) and a higher emissivity in comparison to the C/ZrB_2–SiC composite. The two composites exhibited the good ablation-resistive properties with no obvious erosion rate after the arc-heated wind tunnel ablation tests. The surface of the C/SiC composite appeared to be coarse and had many rounded protrusions while a denser and more homogeneous glass oxide scale was formed for the C/ZrB_2–SiC composite. The maximum surface and back side temperatures of the C/ZrB_2–SiC composite were about 50 °C lower than those of the C/SiC composite, respectively, which was mainly attributed to the evaporation of the B_2O_3 as well as its higher TC.

1. Introduction

Carbon fiber reinforced silicon carbide matrix composites (C/SiC) have been extensively studied due to their good high-temperature strength, high hardness, low thermal expansion, high thermal conductivity (TC), good thermal shock, and good oxidation and ablation resistance [1–3]. These properties make them particularly attractive for potential propulsion and aerospace applications as structural and ablation-resistive components, such as turbopump rotors, nozzle exit ramps, re-entry heat shields, rocket nozzles, and leading edges. However, the C/SiC composites can withstand exposure to an oxidizing environment up to 1650 °C for aerospace applications since the SiC matrix has an inherent limit due to the transition from the passive to active oxidation that occurs below 1700 °C [4,5]. Therefore, it is necessary to look for new materials with the ability to operate at higher temperatures and with improved ablation resistance.

Ultra-high-temperature ceramics (UHTCs), are a family of compounds that are chemically and physically stable at high-temperature (e.g. above 1800 °C) and in oxidizing atmosphere (e.g. monatomic oxygen), which mainly include the borides, carbides, and nitrides of the early transition metals like hafnium, zirconium and tantalum. The characteristics of UHTCs, such as extremely high melting temperature and hardness, retained strength at high-temperatures, as well as good thermal shock resistance and modest thermal expansion, allow these materials as potential candidates for extreme environments associated with hypersonic flight and rocket propulsion [6–9]. Especially, refractory metal diborides such as ZrB_2 and HfB_2 are considered as candidates for hypersonic vehicle aerospaces, such as engine cowl inlets, wing leading edges and nosecaps, because the high melting points of these materials coupled with their ability to form refractory oxide scales give them the capability to withstand temperatures in the 1900–2500 °C range [10]. The addition of SiC has improved the oxidation resistance of Zr(Hf)B_2 between 1000 °C and 1800 °C due to the formation of less volatile silica-containing scales [11]. Although these materials Zr(Hf)B_2–SiC are being developed, they are less mature at this time and are still facing many barriers, such as poor sinterability and/or bulk-forming techniques, low fracture toughness and poor thermal shock resistance [12,13]. A possible approach to enhance their mechanical properties is to introduce carbon fibers as a toughening and strengthening phase since the fibers can be used at ultra-high-temperature beyond 1800 °C.

Therefore, the introduction of ZrB_2 into C/SiC composites is a possible route to further improve their oxidation-resistive and ablation-resistive properties; on the other hand, it is also likely that the ZrB_2–SiC ceramics will benefit from the incorporation of a carbon fiber reinforcement phase in order to improve the fracture toughness, impart an acceptable level of the thermal shock, and lower the density. In this investigation, the ZrB_2 particle was introduced into the C/SiC composite in order to improve the ablation resistance while the major composition of the matrix is the SiC. The work about ZrB_2–SiC ceramics reinforced by carbon fibers with a large amount of ZrB_2 will be continued.

In this paper, the C/SiC and C/ZrB_2–SiC composites were prepared by a novel chemical vapor infiltration technique (CVI) using a fiber preform and a powder-fiber preform, respectively, and their

* Corresponding author. Tel./fax: +86 24 83978236.
E-mail address: jydeng@imr.ac.cn (J. Deng).

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TC, specific heat capability and emissivity were compared. In addition, their ablation behaviors were also analyzed and compared using an arc-heated wind tunnel test with a flame temperature over 2000 °C. Arc-heated wind tunnel testing represents the best ground-based simulation of a re-entry environment, in different ways; and it provides the possibility to explore the oxidation behavior of these materials under extreme conditions.

2. Experimental

2.1. Composite fabrication

In the present work, a four-stage process was used to fabricate the C/SiC and C/ZrB_2–SiC composites. At first, a 2D-preform of the C/SiC composite was fabricated by alternately stacked weftless plies and short-cut-fiber webs using a needle technique. The fiber content of the preform was 30.6 vol.%. The preform used to prepare the C/ZrB_2–SiC composite had alternately stacked layers of ZrB_2 powder (1.5 μm), short-cut-fiber webs, and weftless plies, which were needle punched in the *Z*-direction. The fiber content was 24.9 vol.% and that of the webs was 3.7 vol.%; and the ZrB_2 content was 3.9 vol.%. For the different preforms, the successive weftless plies were oriented at an angle of 90°, and the carbon fiber types used were PAN-base T700 carbon fiber with a 12 k tow, produced by Toray Co., Japan [14]. Secondly, the two preforms were clamped in a graphite clamp with purposes of degumming the carbon fibers and maintaining the preform shape. The processing temperature was increased to 1200 °C and kept there for 2 h in an argon atmosphere. In the third stage, the preforms were consolidated by forming a small amount of pyrocarbon (PyC), which was produced by the pyrolysis of natural gas over 10 h at 1000 °C in an isothermal CVI apparatus. The preforms were rapidly densified by forming a SiC matrix by a novel CVI technique. The preforms were clamped between two graphite electrodes for directly heating by passing an electric current in a cold wall and normal-pressure furnace [15]. The final densities of the C/SiC and C/ZrB_2–SiC composites were 2.2 g/cm^3 and 2.4 g/cm^3, respectively.

2.2. Tests and characterization

TC tests were carried out using a flash method through $\Phi 12 \times 2.5$ mm samples on a FlashlineTM-5000 thermal properties analyzer. The thermal diffusivity and the specific heat capability can be obtained from the tests, and the TC was computed from the measured thermal diffusivity and specific heat, multiplied with the bulk density measured by an Archimedes method. Emissivity was obtained using a Fourier transform infrared spectrometer in the temperature range 200–800 °C on disc-shaped samples, 60 mm in diameter and 6 mm thick. The radiation energies of the specimen and the blackbody at the same temperature were measured. The emissivity was calculated by dividing the radiation energy integral of the specimen by that of a blackbody in the wavelength range of 8–14 μm.

The ablation response was determined using an arc-heated wind tunnel test. The working principle of the test is similar to that of an electric arc welding machine widely used in industry. High pressure cool air was heated and ionized to form a plasma between the two electrodes of the arc heater by applying high voltage and a strong current. The air plasma was accelerated to hypersonic speed using a converging–diverging nozzle. The temperature of the air plasma can be adjusted by controlling the electric current. The schematic assembly is illustrated in Fig. 1. Before the ablation test, the back side of each flat specimen (100/76/7 mm) was attached to an insulation layer with an inorganic binder. The specimen with the insulator was placed in the outlet of a hypersonic nozzle and had an angle of 10° with the axis of the nozzle. The surface temperature of the specimen was monitored by a non-contact infrared pyrometer and the flame temperature was estimated to be over 2000 °C. The back side temperatures of the specimen with the insulator were measure by three thermocouples at different points. Two tests were carried out for each composite. The ablation process included two continuous stages: heat enthalpy 14.3 GJ/kg, cold wall heat flux 280 kW/m^2, Mach number 3.5, heat time 300 s; heat enthalpy 10.3 GJ/kg, cold wall heat flux 140 kW/m^2, Mach number 3.5, heat time 350 s. In the experiment, the low heat flux was used since the major composition of the composites was the SiC matrix.

The microstructure and the composition of the C/SiC and C/ZrB_2–SiC composites before and after the ablation tests were explored by a scanning electron microscope (SEM) combined with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the composites

The cross-sectional microstructures of the C/SiC and C/ZrB_2–SiC composites are presented in Fig. 2 and the microstructures with a larger magnification in the web region are shown in Fig. 3. For the C/SiC composite, the SiC matrix and some large inter-layer pores are clearly visible in the webs between the weftless layers; and a large amount of SiC matrix is formed and some inter-fiber pores are residual in the web region. Many ZrB_2 particles, some SiC matrix and a few residual large inter-bundle pores occur in the webs of the C/ZrB_2–SiC composite. The sound SiC matrix integrates the ZrB_2 particles and the carbon fibers through the SiC growth surrounding the particles and fibers.

The volume of the SiC matrix (V_{SiC}) can be calculated in the composite according to the following formula

$$V_{SiC} = \frac{\rho V - \rho_{cf} V_{cf} - \rho_{PyC} V_{PyC} - \rho_{ZrB_2} V_{ZrB_2}}{\rho_{SiC}}$$

where ρ is the bulk density of the composite and ρ_{Cf}, ρ_{PyC}, ρ_{ZrB_2} and ρ_{SiC} are the true densities of the carbon fibers, PyC, ZrB_2 and SiC, respectively, and V, V_{Cf}, V_{PyC} and V_{ZrB_2} are their volumes. The volume ratio of the ZrB_2 particles and the SiC matrix (V_{ZrB_2}/V_{SiC}) can be

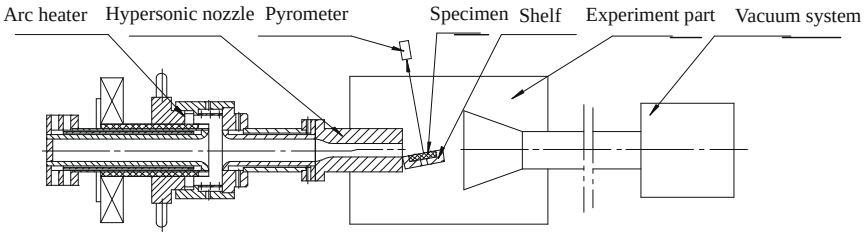

Fig. 1. Schematic presentation of the arc-heated wind tunnel assembly.