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Fabrication of gradient C/C-SiC-$MoSi_2$ composites with enhanced ablation performance

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ABSTRACT

C/C-SiC-$MoSi_2$ composites with gradient composition and microstructure were prepared by a novel vacuum filtration infiltration (VFI) process with a later hydrothermal densification. The composition distribution, microstructure, density, porosity, thermal conductivity and ablation properties of the composites were investigated. Results show that the distributions of SiC and $MoSi_2$ are homogeneous and gradient along the cross-section of the composites, respectively. From the inner part to the outer part of the composites, the increase in density and thermal conductivity is achieved. The outer part of the composites exhibits enhanced ablation performance. After being exposed to the oxyacetylene flame at 2000 °C for 30 s, the linear and mass rates of the as-prepared composites are only 0.0051 mm/s and 0.76 mg/s.

1. Introduction

With the rapid development of hypersonic transportation, reentry vehicles and propulsion applications, there generate great challenges for ultra high temperature materials used in thermal protection systems (TPS) recently. Typical operating temperatures of TPS panels are 1000–1500 °C [1], carbon fibers reinforced carbon (C/C) composites are desirable candidates for thermal protection systems because of their excellent properties at elevated temperatures, low density and low coefficient of thermal expansion (CTE) [2–5]. However, the poor anti-oxidation property of C/C will lead to the poor ablation resistance. In order to improve the ablation performance of C/C, many works have been focused on introducing ultrahigh temperature ceramics (UHTCs) such as SiC [6,7], ZrC [3,8], ZrB_2 [9], ZrC-SiC [10,11] and ZrB_2-SiC [12,13] into C/C composites through multiple approaches. And the ablation resistance of C/C was effectively improved. But little work about using $MoSi_2$ to enhance the ablation property was reported though $MoSi_2$ possesses excellent high temperature performance, such as high melting point (melting point 2030 °C), high thermal conductivity (42 W m^{-1} K^{-1} at 500 °C), good oxidation and corrosion resistance at high temperatures [14–16]. In addition, $MoSi_2$ can be oxidized to form molten state SiO_2 slowly, and the molten SiO_2 can effectively heal the defects and protect the carbon matrix [17–20]. So $MoSi_2$ is a potential candidate for improving the ablation property of the C/C composites.

In previous researches, multi-layer heat resistant materials were used in the TPS design proposals [21], but the interface bonding of above-mentioned materials will affect the reliability of space vehicles. In order to solve the interface bonding problem and improve the utilizing rate of materials, feasible solutions for TPS are developed from single heatproof scheme to thermo-structure integration, which provides many advantages such as excellent interface bonding, light weight, high efficiency and similar CTE with the cold part (inner part) [22–24].

As a result, high temperature materials will be enriched in the dense side (outer part) of the gradient composites. Because of the compact structure and higher thermal conductivity, it can transmit heat and bear elevated temperature ablation. The cold side (inner part) is porous, which has a lower thermal conductivity coefficient [25]. Therefore, excessive heat cannot be transferred to the inner part of TPS.

In the present work, the C/C-SiC-$MoSi_2$ composites with gradient structure and composition were developed by using a vacuum filtration infiltration (VFI) process with a later hydrothermal densification. The composition distribution, microstructure, density, porosity, thermal conductivity and ablation resistance of the composites were particularly investigated.

2. Experimental

2.1. Fabrication of the composites

The preforms (carbon fiber felts, 0.17 g/cm^3) were cut into small

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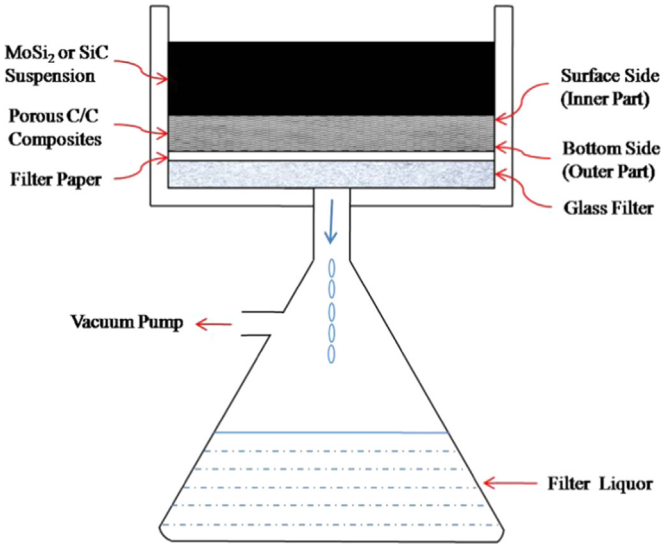

Fig. 1. Schematic of the vacuum filtration infiltration process.

specimens (35 × 10 mm) and densified to 0.24 g/cm^3 with a hydrothermal process at 200 °C for 6 h by using 1 mol/L glucose aqueous solution as media. After that, the porous specimens were cleaned ultrasonically with distilled water and dried at 100 °C for 4 h, then fixed in a glass filter.

1.5 g of SiC (particle size 0.5–0.7 μm, purity ≥ 99.9%) and 2.5 g of $MoSi_2$ (particle size 1–3 μm, purity ≥ 99%) were dispersed respectively in 50 ml isopropanol with an ultrasonic bath for 30 min (the ultrasonic power was kept at 100 W) and a later magnetic stirring for 24 h. The SiC suspension and $MoSi_2$ suspension were then forced to penetrate through the low density C/C composites successively by the VFI process as illustrated in Fig. 1. The contents of SiC and $MoSi_2$ in the composites were controlled by the deposition times and cycles.

After 12 times VFI process (firstly 4 times SiC infiltration and then 8 times $MoSi_2$ infiltration), the specimens were soaked into the saturated solution of glucose (at room temperature). Next, the composites were hydrothermal treated at 200 °C for 12 h. This soaking with a later hydrothermal treatment was repeated for 10 times in order to improve the density of the composites. Finally, they were carbonized at 1200 °C for 2 h in an argon atmosphere to achieve C/C-SiC-$MoSi_2$ composites. Pure C/C composites were also prepared by the same hydrothermal and carbonize processes without infiltrating SiC and $MoSi_2$ particles.

The whole bulk density of C/C-SiC-$MoSi_2$ composites was controlled to about 1.72 g/cm^3. The total mass fraction of SiC and $MoSi_2$ particles was about 48.7%, while the mass ratio of SiC/$MoSi_2$ was kept at 1/4. The volume percentage of $MoSi_2$ and SiC ($VSiC/MoSi2$) was 18.6%, which were calculated by Eq. (1).

Where $D_{C/Filler}$, D_{Felt} are the densities of carbon fiber felts after the VFI process, carbon fiber felt, respectively; $D_{SiC/MoSi2}$ is the mean density of SiC and $MoSi_2$ particles. The density and porosity of each part in C/C-SiC-$MoSi_2$ composites will be discussed in the discussion section.

2.2. Testing and characterizations

The ablation test of the specimens was carried out with an oxyacetylene torch flame. During the test, the distance between the specimen surface and the nozzle of flame gun was kept at 15 mm. The ablation angle was 90°. The flame width was 3–5 mm, and the inner diameter of the nozzle was about 2 mm. Six specimens were exposed to the oxyacetylene flame for 30 s The average linear and mass ablation rates of the composites were calculated according to Eqs. (2) and (3).

Where R_l is the linear ablation rate; Δd is the change of the sample's thickness at the most serious ablated region before and after ablation; R_m is the mass ablation rate; Δm is the sample's mass change before and after ablation; t is the ablation time.

The phase composition and morphology of samples before and after ablation were characterized by X-ray diffraction (XRD, Rigaku D/max-3C) and scanning electron microscope (SEM, JSM-6390A) combined with energy dispersive spectroscopy (EDS). The thermal conductivity of the composites was evaluated by laser flash on a LFA-427 thermal conductivity meter. The open porosity of the composites was measured by a mercury injection apparatus (micromeritics-Auto pore IV 9500).

3. Results and discussion

3.1. Phase composition and microstructure of the composites

As is shown in Fig. 2, the main phases of the composites are β-SiC and $MoSi_2$, which is well in accordance with the experimental design. This indicates that the SiC and $MoSi_2$ particles were successfully introduced into porous C/C composites by the VFI process. In addition, no peaks of carbon are observed, inferring that the amorphous carbon fiber felts were used.

Fig. 3 shows the backscattered electron images and EDS analysis of the as-prepared C/C-SiC-$MoSi_2$ composites. Clearly, homogeneous and dense surface without any defects is achieved (Fig. 3a). By the cross-section SEM image of the as-prepared composites (Fig. 3b), the outer part exhibits dense structure although some small pores are found. The pores may be generated by the polishing before the SEM observation. From the magnified image of the cross-section microstructure (Fig. 3d), two kinds of crystallites with different color can be observed among the carbon fibers. The EDS analysis shows that the grey one is composed of Mo and Si elements (Fig. 3e), while the dark one is composed of C and Si elements (Fig. 3f). Combined with the XRD results (Fig. 2), it can be confirmed that the grey one is $MoSi_2$ and the dark one is SiC. These demonstrate that the pores of the porous C/C preform were filled with $MoSi_2$ and SiC particles during the VFI process

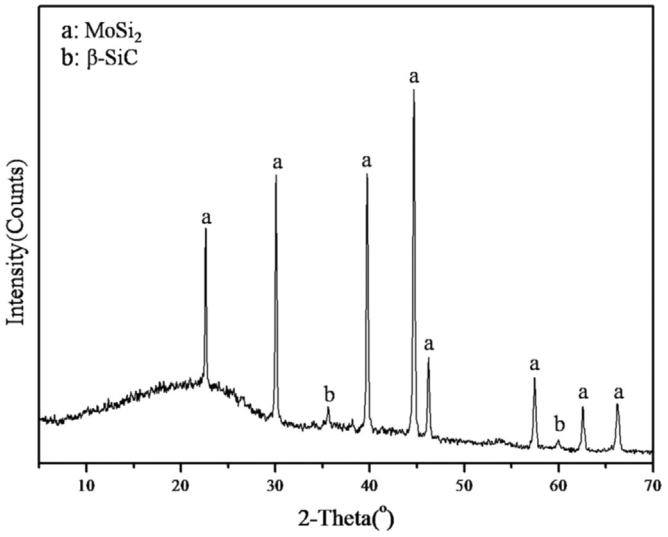

Fig. 2. XRD pattern of the as-prepared C/C-SiC-$MoSi_2$ composites.