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Free standing graphene/SiC films by *in-situ* carbothermal reaction as thermal shielding materials

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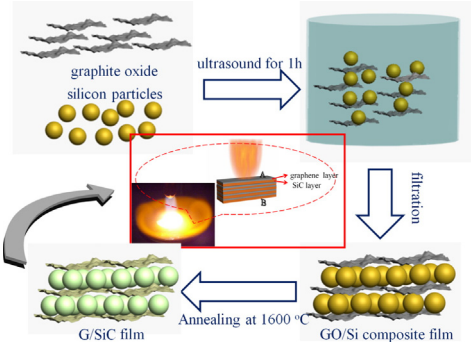
HIGHLIGHTS

- Free-standing Graphene/SiC film was prepared by one step *in-situ* carbothermal reaction with graphene oxide/Si film as precursor.
- Graphene/SiC film shows the best anti-ablation performance and mechanical properties when the weight ratio of graphene oxide and Si is 3:1.
- In-plane and out of plane thermal conductivity of graphene/SiC film are 27.98 $Wm^{-1} K^{-1}$ and 0.15–0.23 $Wm^{-1} K^{-1}$, respectively.
- After removing graphene layer, hardness and elastic modulus of Graphene/SiC film were reduced to from 0.56 Gpa to 0.001 Gpa and from 3.40 Gpa to 0.043 Gpa, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Effective thermal shielding materials with perfect anti-ablation and mechanical performances play a pivotal role of protecting aircraft suffering harsh conditions. With graphene oxide (GO) and nano-silicon spheres as raw material, a layered Si/GO precursor film was prepared by filtration, followed by *in-situ* carbothermal reaction to obtain the composite film of SiC and graphene (SiC/G film). The as-obtained material shows a sandwich-like anisotropic structure, with excellent anti-ablation performance in ablation experiment. The film exhibit a high mechanical stiffness with hardness and elastic modulus of 0.56 and 3.40 GPa, respectively. Besides, in- and out-plane thermal conductivity are 27.98 and 0.15–0.23 $Wm^{-1} K^{-1}$, respectively. In the film, the orientated graphene sheets are not only the scaffold to retain the integrity of the film, but also improve in-plane thermal dissipation efficiency. Meanwhile, *in-situ* grown SiC particles act as the major anti-ablation functional layer, as well as the interlayer spacer to retard the heat transfer perpendicular to the film. Therefore, this novel sandwich-like structure composed by SiC and graphene layers could offer great protection from multiple ablation shocks in many fields.

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1. Introduction

Thermal shielding materials, which are widely employed in reusable space vehicles and high temperature furnaces, must be able to withstand high temperature oxidation and ablation, high heat flux and keep excellent mechanical stress during service process [1,2]. Any material failure in such a harsh environment may cause serious loss and even disaster. Therefore, thermal shielding materials are located in the center stage of these fields.

Carbon materials, such as carbon fiber, graphite fiber, graphite block and carbon felt, as the traditional thermal shielding material, have received much attention due to their excellent high-temperature strength, low coefficient of thermal expansion and good thermal shock resistance [3,4]. However, pure carbon material cannot hold in oxidizing atmosphere or ablation environment beyond 400–500 °C [5,6]. One way to solve the problem is coating silicon carbide (SiC) layers on the surface of carbon matrix [7–9], which is attributed to its excellent thermal and chemical stability, high thermal conductivity and strength retention at high temperature [10,11].

Some literatures [12–14] demonstrate that SiC could be synthesized *via* carbothermal reaction with nano-silicon powder and carbon source as precursors, at a temperature ranging from 1400 to 1800 °C. In our previous work, thermal reduced graphene (TRG) was reported as an effective carbon source for high quality SiC nano-whiskers through carbonthermal reaction with silicon nanoparticle [14]. However, the synthesized SiC could not assemble a film. Meanwhile, graphene, a two-dimensional carbon crystal comprises of sp^2-hybridized carbon atoms arranged in a hexagonal lattice [15], is very easy to be assembled film materials [16]. It has been demonstrated that GNP has high potential to improve mechanical properties of composites [17]. A sandwich structural Si nanoparticle-graphene oxide composite film has been prepared for using as Lithium-ion batteries [18]. Thus, it is considered that SiC could combine with graphene to prepare a film with multilayered hierarchical structure, which would be a fresh attempt for graphene in thermal shielding field. For the layered film materials, graphene could be used as carbon source and scaffold for assembling graphene/SiC (G/SiC) film simultaneously. Zhao et al. [19] have prepared Si nanoparticle-graphene oxide paper composites through a filtration-directed assembly approach. Based on the above researches, multilayers hierarchical structural G/SiC film could be fabricated through annealing GO/Si composite film at a suitable temperature. During the process, part of GO is used as carbon sources react with silicon for obtaining SiC, meanwhile the remaining GO sheets is reduced to graphene act as a mechanical support skeleton to assemble a film.

In this contribution, we try to design a kind of novel multilayered sandwich-type G/SiC composite film, with graphene and SiC as the repeatable building blocks, and explore its application in multiple ablation and oxidation protection fields. It could still sustain the intact structure even the surface damaged, owing to the protection of sub-surface SiC. The film was prepared by a facile *in-situ* carbothermal reaction with GO/Si multilayered sandwich-type composite film as precursor. The results of oxygen-acetylene ablation experiments demonstrate that the above prepared film has remarkable performance for multiple thermal shielding. The concept of design of multilayered sandwich-type composite film could pave a way for the preparation of thermal shielding materials in future.

2. Experimental

2.1. Preparation of G/SiC film

The graphite oxide was prepared from natural graphite powder by a modified Hummers method [20]. In a typical synthesis of GO/Si nanocomposite suspension, 0.03 g of siliconnano-particles and 0.09 g of graphite oxide were dispersed in deionized water (20 mL) by ultrasound for 1 h. The resulting homogeneous aqueous dispersion was filtrated to get GO/Si composite film. G/SiC film was obtained by drying GO/Si composite film at room temperature for 24 h, followed by annealing at 1600 °C for 1 h under Ar atmosphere with a heating rate of 5 °C min^{-1}.

2.2. Characterization

The as-fabricated film was characterized by using JEM-2010 high resolution transmission electron microscope (TEM), atomic force microscopy (AFM, NanoWizardIII, JPK Instruments), JSM-7001F field emission scanning electron microscope (SEM), thermo-gravimerticanalysis (TG,TA Q600 instrument), XRD (D8 Advance diffractometer with Cu Kα radiation), a Fourier transform infrared spectrometer (FT-IR, Magna-IR 750, Nicolet, US). The thermal diffusivity was determined using Laser Flash Apparatus (NETZSCH LFA 447 NanoFlash) operated at room temperature. For the measurement of in-plane thermal diffusivity, film was punched out as a wafer with 25.4 mm diameter. Then the sample was brought into a special sample carrier with 25.4 mm diameter(Fig. 1 in ref. [21]). During test process, specific parameters were set as following: Pulse Width was set as 0.31 ms, Main amp was set as 25,200, duration was set as 700 ms. At the same test condition, out of plane thermal diffusivity was measured with a wafer of 12.7 mm diameter. Then the sample was brought into a special sample carrier with 12.7 mm diameter (Fig. 2 in ref. [21]).

The specific heat (C_P) used in this paper was measured by differential scanning calorimeter (DSC, 200F3). The thickness (h) of these films was measured with SEM. The weight change of the film was investigated by a high accuracy electronic balance (SHIMADZU). The ablation performance was characterized by oxy-acetylene torch. Specimens were placed in a direction vertical to the flame. The illustration of the experiment was shown in Fig. 3 in ref. [21]. the specific ablation test parameters were as shown below: O_2 gas flux was 36 L/h, C_2H_2 gas flux was 22 L/h. The ablation time is 60 s. Mechanical properties were characterized by Nanoindentor (Nano G200).

3. Results and discussion

GO was prepared with lateral size of 1–2 μm (Fig. 1a) and thickness of 1.71 nm (Fig. 1b) by a modified Hummers method. The size of silicon particles were 50–80 nm (Fig. 1c). GO/Si film (Fig. 1d) was obtained by vacuum filtrating mixed solution of Si nano-particles and GO hydrosol. SiC/G film (Fig. 1e) was prepared by annealing GO/Si film at 1600 °C under argon atmosphere. The cross-section image of GO/Si film was shown in Fig. 1f, silicon particles were wrapped by GO sheets. After annealing treatment, G/SiC film is obtained with uniform controllable thickness (Fig. 1g) and SiC particles surrounded by graphene sheets (Fig. 1h). Meanwhile, the composite film is in obvious sandwich-like structure. This typical anisotropy structure may make the film excellent property.

The phase components of G/SiC film are confirmed by X-ray diffraction (XRD) characterizations (Fig. 2a). It is found that the typical diffraction peaks of Si (28.4°, 47.3°, 56.1°, 69.1°and76.4°: JCPDS 27-1402) disappeared for GO/Si film while the diffraction peaks of β-SiC (35.6°, 41.4°, 60.0°, 71.8°and 75.5°: JCPDS 29-1129) appeared after annealing. Meanwhile, the results show clearly that GO sheets ($2\theta = 12.5°$) have been effectively exfoliated and transformed into graphene ($2\theta = 26.46°$). Fig. 2(b) shows FT-IR spectrum of G/SiC film. The strong peak at 838 cm^{-1} corresponds to the stretching mode of Si-C bond [22], which indicates the existence of SiC for G/SiC film.

In order to further verify the mass fraction of the compositions (SiC, graphene, SiO_x) in G/SiC film, some works were done as following. SiO_x may origin from silicon that reacted incompletely. Firstly, G/SiC film (m_1) was immersed in hydrofluoric acid (HF) for 24 h to remove the amorphous SiO_x, followed by washing repeatedly with deionized water until the pH was 7 and dried at 110 °C to get the sample (m_2). Then, m_3 was obtained by annealing m_2 in air at 800 °C for 60 min.