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Short Communication

Fabrication and thermal shock resistance of in situ SiC nanowire-SiC/SiC coating for carbon/carbon composites

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ABSTRACT

To improve toughness of SiC outer layer produced by chemical vapour deposition for carbon/carbon composites, in situ SiC nanowires on SiC inner layer were prepared by pack cementation. SiC nanowires were distributed uniformly on SiC inner layer, and SiC was filled in the interspace of SiC nanowires to form a dense SiC outer layer. After introducing SiC nanowires, the size of cracks in SiC outer layer decreased and the weight loss of coated carbon/carbon samples decreased from 127.7 g m^{-2} to 76.2 g m^{-2} after 40 times thermal cycling between 1773 K and room temperature.

1. Introduction

Carbon/carbon (C/C) composites are important thermal structure materials in the aircraft and aerospace industry, because of their high strength-to-weight ratio, resistance to thermal shock and retention of strength at high temperature [1,2].

However, C/C composites are prone to oxidation at temperature above 723 K, which limits their use at high temperatures [3–5]. Applying multilayer coatings, such as SiC/glass [6], SiC/Si–Mo [7] and SiC/mullite [8], have been proved as one of the best methods to solve the problem. In these coatings, SiC coating is a common ground for the internal buffer layer owing to its excellent oxidation resistance and good compatibility with C/C substrates [9,10]. However, the multilayer coatings always encounter failure because of cracks coming from mismatch of thermal expansion coefficient (CTE) between SiC layer and outer layer during thermal shock. So reinforcement materials should be introduced into the outer layer to improve their toughness. It is reported that [11] the yield strength of SiC nanowires (NWS) could be up to over 50 GPa which is lager than those of micro-scale SiC whiskers/fibres. Therefore, SiC NWS have attracted more attentions for using in coatings as the reinforcements [12]. Up to now, several techniques were demonstrated to produce SiC NWS, including carbon nanotubes-confined growth [13], chemical vapour deposition (CVD) [14–16], carbon-thermal reduction [17–19], and polymeric precursor pyrolysis [20], etc. However, most of these methods involved complex processes and manipulation.

This work reports a simple and low cost synthetic route to prepare SiC NWS by pack cementation. Both SiC NWS and SiC coating were formed on C/C composites through this method. This coating could be applied as the internal buffer layer, and SiC NWS on SiC coating could also toughen the outer layer. Therefore, a new SiC nanowire-SiC (SiC NW-SiC) coating was prepared by pack cementation to improve the toughness of SiC outer layer produced by CVD for C/C composites. The microstructures and thermal shock resistance of the coatings were investigated.

2. Materials and methods

The specimens ($10 \times 10 \times 10$ mm^3) used as substrates were cut from bulk two dimensional C/C composites with a density of 1.75 g cm^{-3}. The specimens were abraded with 400 grit SiC paper, then cleaned with ethanol and dried at 373 K for 2 h. Powder compositions for the pack cementation process were given as follows: 65–75 wt.% Si, 10–25 wt.% graphite, 5–8 wt.% Al_2O_3 and 5–15 wt.% ferrocene. All the powders were analytical grade and had the particles size below 300 mesh. They were mixed by a magnetic stirrer for 2 h. The pack mixtures and C/C specimens were put in a graphite crucible, and then heat-treated at 2073–2373 K for 2 h in an argon protective atmosphere to form the SiC NW-SiC coating. For comparison, SiC coating without SiC NWS was also prepared by removing ferrocene in the powder compositions with a similar process. Then the SiC NW-SiC coating coated C/C composites were hung in a vertical CVD furnace by a bundle of carbon fibres to deposit SiC outer layer. The deposition was performed at 1373 K for 24 h at reduced pressure of 1 kPa using methyltrichlorosilane (MTS, CH_3SiCl_3) with a H_2:MTS molar ratio of 15 which was achieved by bubbling hydrogen gas through the MTS. Argon was

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used as diluent gas during deposition to slow down the chemical reaction rate.

Thermal shock resistance tests of the coatings were carried out between 1773 K and room temperature in air by natural convection in a corundum tube furnace [21]. The specimens were put into an electrical furnace at 1773 K for 3 min, followed by a cooling process outside the furnace at room temperature for 3 min. The heating and cooling rates were 8 K/s and 7 K/s respectively. After being weighted, the specimens were put directly into the furnace again for the next oxidation period. The thermal shock test was then repeated for 40 cycles. Weight changes of the samples after every thermal cycle from high temperature to room temperature were obtained by a precision scale and recorded as a function of thermal cycle. The weight loss (ΔL) was calculated using Eq. (1).

$$\Delta L = \frac{m_0 - m_1}{S} \tag{1}$$

where m_0 is the original mass of coated C/C composites; m_1 is the mass of the coated C/C composites after oxidation at high temperature; and S is the surface area of the sample [22]. Five samples for each kind of sample were tested and the final weigh losses were obtained by computing the average values of five samples.

The morphology and crystalline structure of the as-received coatings were analysed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 1a shows the typical SEM image of the SiC NW-SiC coating on C/C composites. The NWS were deposited uniformly on SiC coating of C/C composites. It can be seen from Fig. 1b that the random oriented NWS are several nanometres to hundreds of nanometres in diametres and tens of micrometres in length. The NWS wrap each other with straight or curved morphology. The XRD pattern of the coating (Fig. 1c) shows that all of the strong intensity peaks could be indexed to the β-SiC structure with a low-intensity peak marked with S.F., which may be due to the stacking faults in the SiC NWS [23–25].The TEM image and SAED pattern of an individual nanowire are shown in Fig. 2a. The SAED pattern indicates that the NW consists of β-SiC structure, companying with α-SiC structure. By calculation, the diffraction is consistent with (1 1 0) crystal band of β-SiC, which consists of $(1\bar{1}1)$, $(1\bar{1}\bar{1})$ and (0 0 2) crystal planes. The diffraction of α-SiC is consistent with (1 0 0) crystal band, composed of (0 1 0), $(00\bar{2})$ and $(01\bar{1})$ crystal planes. Fig. 2b shows the EDS analysis result of the middle part of the NW. Only Si and C are detected which indicates a pure SiC composition is formed in NWS. The existence of Fe besides Si and C (Fig. 2C) is confirmed by EDS analysis of the tip of the NW. A spherical cap at the tip of NW and Fe observed in the cap imply that the NWS are formed by vapour–liquid–solid (VLS) mechanism. The whole growth process of SiC NWS can be generally described as reactions (1) and (2):

$$\mathrm{Si(s)} \rightarrow \mathrm{Si(g)} \tag{1}$$

$$\mathrm{Si(g)} + \mathrm{C(s)} \rightarrow \mathrm{SiC(s)} \tag{2}$$

At a high reaction temperature, Fe is formed to nanosized liquid droplets due to the decomposition of ferrocene as a catalyst metal. These droplets are favourable sites for the further growth of SiC nanostructures. At the same time, solid Si is evaporated at high temperature to generate Si vapour, and the Si vapour reacts with graphite powder to form SiC clusters. Controlled by the VLS mechanism, the SiC clusters would continuously precipitate out from the liquid Fe droplets to form SiC NWS.

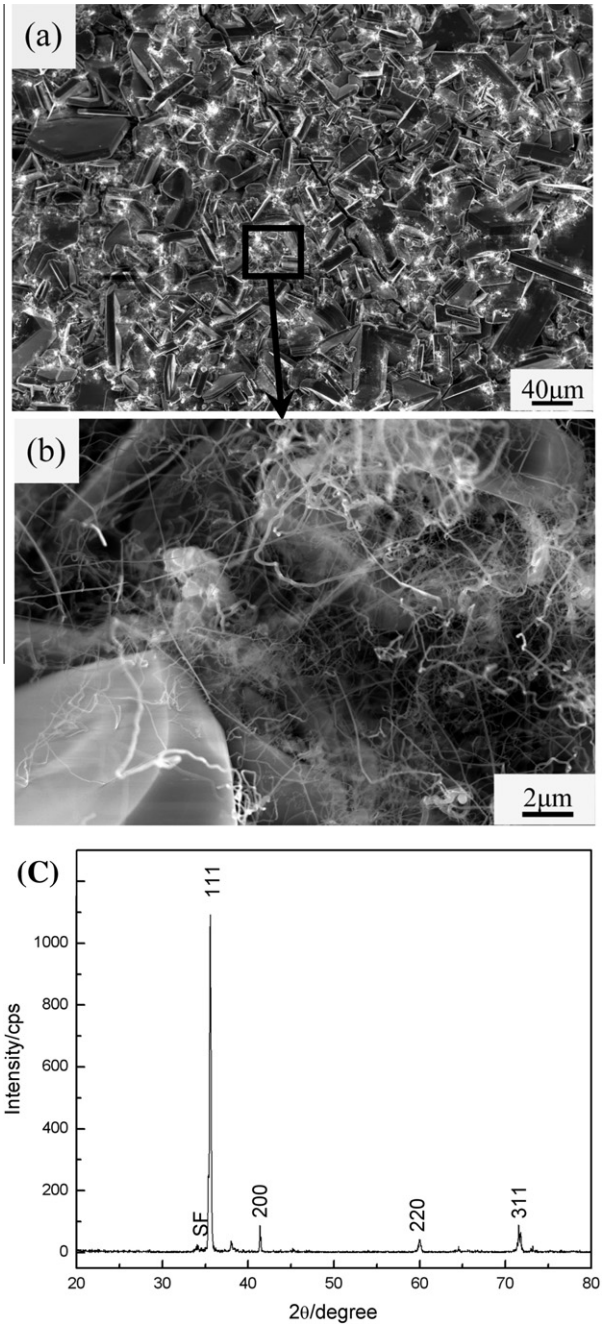

Fig. 1. The SEM images (a), (b) and XRD pattern of the SiC NW-SiC coating.

It is well known that the toughening mechanism of SiC NWS should be pulling-out and bridging of NWS and crack deflection. To verify the toughening effect of the SiC NWS, a SiC outer layer was produced by CVD on SiC coated C/C composites with and without SiC NWS (Fig. 3). From the comparison between the two coatings, it was found that the crack widths are 8 ± 1.5 μm for SiC/SiC coated C/C composites and 1.5 ± 0.5 μm for SiC NW-SiC/SiC coated C/C composites, respectively. Therefore, the cracks in SiC outer layer with NWS are smaller in width than that in SiC outer layer without NWS. That is to say, the SiC NWS in SiC outer layer could effectively prevent the formation of cracks generated from thermal stress.

To further test the toughening effect of SiC NWS, the thermal shock resistance tests were carried out. Fig. 4 shows the thermal shock resistance results of the two kinds of coatings. It is found