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Synthesis and toughening effect of SiC nanowires wrapped by carbon nanosheet on C/C composites

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ABSTRACT

SiC nanowires wrapped by carbon nanosheet have been synthesized by chemical vapor deposition using methyltrichlorosilane as precursor at standard atmospheric pressure. The morphological and structure of as-received products were characterized. The nanowires consist of a single-crystalline β-SiC core and a carbon nanosheet shell. The diameter of β-SiC core is about 30 nm. The thickness of carbon nanosheet is about several nanometers. The carbon nanosheet is polycrystalline graphite. EELS analysis of different elements in nanowires further prove that the nanowires are carbon nanosheet wrapped SiC nanowires. To verify its toughening effect, SiC coating has been also deposited in the porous carbon nanosheet wrapped SiC nanowires layer by chemical vapor deposition at low pressure. The thermal shock tests showed that the weight loss of SiC nanowires wrapped by carbon nanosheet-toughened SiC coated C/C composites was only 2.38% after 25 times thermal cycling between 1773 K and room temperature. The incorporation of carbon nanosheet wrapped SiC nanowires can effectively improve the toughness and thermal shock resistance of SiC coating on C/C composites via cracks pining and deflection.

1. Introduction

SiC are widely used as structural materials due to their high mechanical strength, high hardness, low density, high thermal conductivity, low thermal expansion coefficient, and excellent oxidation and corrosion resistances [1–4]. Compared with bulk and micro-sized SiC structures, SiC nanostructures have several novel mechanical, electrical and optical properties because of their reduced size [5–9]. According to Wong et al. [5], SiC nanorod has an estimated yield strength of over 50 GPa, substantially higher than that of bulk SiC. Therefore, one-dimensional SiC materials are commonly used as reinforcement materials for ceramics [10,11]. However, most of them have smooth outward appearance. As we all know, the more complex of SiC nanostructures, the better it would be anchored in their embedding matrix than the smooth ones when used in composites [12]. More recently, several kinds of complex SiC nanostructures have been successfully synthesized. For instance, Wang et al. [13] synthesized periodically twinned SiC nanowires by the carbonthermal reduction of a carbonaceous silica xerogel at 1573 K. Wei et al. [14] reported the growth of necklace-like SiC nanowires via the reaction of SiO_2 and graphite powders without any catalyst at 1673 K. Guo et al. [15] prepared SiC nanowires with fins by CVD in a vertical vacuum furnace at 1623 K using a powder mixture of milled Si and SiO_2 and gaseous CH_4 as the raw materials. To the best of our knowledge, the synthesis of carbon nanosheet wrapped SiC nanowires has not been reported.

In this letter, we reported a new form of carbon nanosheet wrapped SiC nanowires synthesized by CVD using methyltrichlorosilane (MTS, CH_3SiCl_3) as precursor at atmosphere pressure. The structure and morphology of the SiC nanowires were investigated. To prove the toughening effect of as-synthesized SiC nanowires on the C/C composites, SiC coating was deposited in the porous SiC nanowires layer by CVD at low pressure. Then the indentation test and thermal cycle experiment were carried out to show whether the CVD SiC coating was toughened by the SiC nanowires wrapped by carbon nanosheet and the SiC nanowires wrapped carbon nanosheet had better toughening effect than the SiC nanowires with smooth surfaces.

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2. Experimental

The specimens ($10 \times 8 \times 4$ mm^3) used as substrates were cut from bulk two dimensional carbon/carbon (C/C) composites with a density of 1.70 g cm^{-3}. The specimens were abraded with 800 grit SiC paper, then cleaned with ethanol and dried at 353 K for 2 h. The C/C composites were dipped in the $Ni(NO_3)_2$/ethanol solution (0.001 mol/L). After dried in the air, the substrates were hung in a vertical CVD furnace by a bundle of carbon fibers to deposit the SiC nanowires. After pumping the furnace to a pressure of 2 kPa, high purity argon gas was fed at a flow rate of 1000 ml min^{-1} into the furnace to maintain an inert atmosphere pressure. The furnace was electric-heated with a rate of 10 K min^{-1}. H_2 was used as carrier gas, which transfers MTS through a bubbler to the reactor. Ar was used as diluent gas, which regulates the concentration of the mixture gas. The diluent and carrier gas, containing MTS vapor, were completely mixed before being introduced into the reactor. During depositing process, the MTS bath temperature was kept at 293 K. The flow rates of carrier and diluent gas were 100–200 and 200–450 ml min^{-1}, respectively. During growth, the temperature was held at 1373 K for 1 h under atmosphere pressure. After growth, Ar and H_2 were turned off immediately, which was very important for the growth of carbon nanosheet. Finally, the power was switched off and the furnace was allowed to cool to room temperature naturally. The C/C substrates were covered by a black thick layer which is carbon nanosheet wrapped SiC nanowires layer. The products were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED).

The SiC coating was produced after finishing the SiC nanowires synthesis without taking out the samples by changing the parameters of CVD process. SiC coating was gained at 1373 K for 2 h at low pressure of 1 kPa by using MTS with a H_2:MTS molar ratio of 15. Argon which flow rates was 450–600 ml min^{-1} was used as the diluent gas during deposition to slow down the chemical reaction rate. The SiC coating toughened by SiC nanowires with smooth surfaces was also prepared for comparison in a similar process. The morphology of the surface and fracture surface of the different coatings was characterized by SEM.

To observe directly the toughening effect of carbon nanosheet wrapped SiC nanowires, the indentation test was carried out on the well-polished cross-section of the coating by Micro-indenter (NANOVEA MHT-M) with a diamond Vicker indenter. Load of 2 kg was used to generate the cracks in the indentation area of the coating from where the toughening effect could be directly observed. The morphology of the indentation area was characterized by SEM.

The thermal shock resistance tests of the different coated samples were carried out between 1773 K and room temperature in air flowing by natural convection in corundum tube furnace. The specimens were put into electrical furnace at 1773 K for 3 min, followed by a cooling process out of furnace at room temperature for 3 min and weighted, and then the specimens were put directly into the furnace again for the next oxidation period. The thermal shock test was then repeated for 25 cycles. Cumulative weight changes of the samples after every thermal cycle from high temperature to room temperature was measured by a precision balance and was recorded as a function of time. The mass loss (ML) was calculated using Eq. (1).

$$ML = [(m_0 - m_1)/m_0] \times 100\% \quad (1)$$

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.

3. Results and discussion

The typical SEM image of the black products on C/C composite is shown in Fig. 1(a). It can be seen that large quantities of randomly oriented wire-like nanostructures with rough surface have been synthesized. The magnified SEM image in Fig. 1(a) shows that there is a large number of nanosheet which leads to rough surface of the nanowires. The nanowires are of uniform diameters about 100 nm and length up to several hundreds of micrometers. Fig. 1(b) displays the XRD pattern of the nanowires with rough surface on C/C substrate. In the pattern, the major diffraction peaks indexed with (111), (220), and (311) are consistent with the standard face-centered cubic cell of 3C–SiC (JCPDS card No. 73-1665), which has the lattice constant of a = 0.4349 nm. The strong SiC (111) peak implies the predominant growth along [111] direction of nanowires. The small peak marked with SF is due to stacking faults in the nanowires [16]. Furthermore, the other peaks corresponding to carbon are also found, the intensities of which are much higher than that of SiC peaks. It implies that the carbon peaks not only originate from C/C substrate but also due to the black nanosheet on the surface of nanowires.

In order to characterize the detailed structure of the synthesized

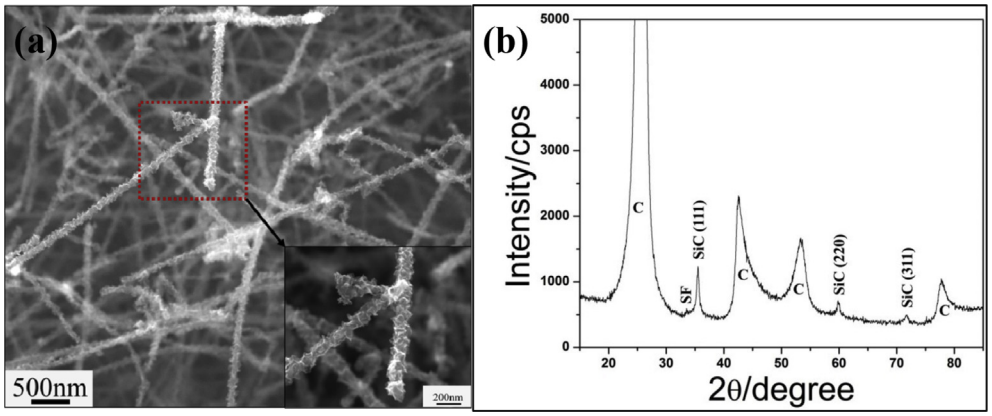

Fig. 1. Typical SEM images (a) and XRD pattern (b) of the obtained products on C/C composites.