Thermal Shock Resistance of SiCNW-SiC Coating for Carbon/Carbon Composites Fabricated by Successive Two-Step CVD Process

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Abstract. The oxidation protective SiC coating toughened by SiC nanowires was fabricated by two-step chemical vapor deposition (CVD) process using MTS as precursor. First, a random-orientation SiC nanowires network was synthesized by atmospheric pressure chemical vapor deposition (APCVD) on carbon/carbon (C/C) composites with Ni assistant. Second, the SiC nanowires network was infiltrated and enwrapped by SiC coating during low pressure chemical vapor deposition (LPCVD) process. The nanowires could effectively toughen the SiC coating by nanowire pullout, nanowire bridging, micro-crack deflection and good interaction between nanowire and matrix interface. The weight loss of SiCNW-SiC coated C/C composites was 2.38% after 25 times thermal cycling between 1773 K and room temperature, while SiC coated C/C composites was 9.50%. The result of the thermal shock showed that the SiCNW-SiC coating had better thermal shock resistance than SiC coating.

Introduction

Carbon/carbon (C/C) composites are important thermal structure materials in the aircraft and aerospace industry due to their low density, high strength-to-weight ratio, excellent thermal shock resistance and non-brittle fracture behavior at elevated temperatures [1]. However, C/C composites are prone to oxidation at temperature above 723 K, which limits their use at high temperatures [2]. To solve this problem, silicon carbide (SiC) coating has been widely used as a coating to provide protection for C/C composites owing to its excellent oxidation resistance and good compatibility with C/C composites [3]. However, SiC coating always encounter failure because of cracks coming from mismatch of thermal expansion coefficient (CTE) between SiC layer and C/C substrate during thermal shock [4]. It is reported that the yield strength of SiC nanowires (NWS) could be up to over 50 GPa which is larger than those of micro-scale SiC whiskers/fibers [5]. Therefore, this work reports a simple method to prepare SiC coating toughened by SiC nanowires through successive two-step CVD process. The microstructure and thermal shock resistance of the SiCNWs-SiC coating were investigated as well.

Experimental

The specimens (10×10×10 mm³) used as substrates were cut from bulk two dimensional carbon/carbon (C/C) composites with a density of 1.78 g cm⁻³. The specimens were abraded with 400 grit SiC paper, then cleaned with ethanol and dried at 373 K for 2 h. The dried C/C substrates were dipped in the Ni(NO₃)₂/ethanol solution (0.001 mol L⁻¹) until no bubbling on it. After that the substrates were dried in air at 373 K for 2 h. The processing steps for fabricating SiCNWs-SiC coating and investigating the microstructure and thermal shock resistance are shown in Figure 1. The substrates were hung in a vertical CVD furnace by a bundle of carbon fibers to deposit the SiCNWs. 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\(^{-1}\). \(\text{H}_2\) was used as carrier gas, which transfers MTS through a bubbler to the reactor. \(\text{H}_2\) was also used as reactant gas which could effectively influence on the product decomposed from MTS. 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, reactant and diluent gas were 100-200, 400-600 and 200-450 ml min\(^{-1}\), respectively. During growth, the temperature was held at 1373 K for 1 h under atmosphere pressure. After SiCNWs growth, the carrier and reactant \(\text{H}_2\) were turned off immediately, and then changed the pressure of the furnace to deposit SiC coating material into as-received porous SiCNWs layer at low pressure CVD (LPCVD) without taking out the SiCNWs coated C/C samples. The specific deposition conditions were as follows: the deposition temperature was 1373 K; the pressure of furnace was 1 kPa, and the flow rates of carrier, reactant and diluent gas were 50-100, 1000-2000 and 400-800 ml min\(^{-1}\), respectively; the deposition time was 4 h. Finally, the power was switched off and the furnace was allowed to cool to room temperature naturally. The C/C substrates were covered by SiCNWs-SiC coating.

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\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. 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 structures of the nanowires and the coatings were analyzed by a scanning electron microscopy (SEM, Tescan TS5136XM) and X-ray diffraction (XRD, SHIMADZU LIMITED XRD-7000s).

**Results and Discussion**

Figure 2(a) shows the SEM image of the as-received nanowires on C/C substrate. It can be seen that nanowires covered the surface of C/C composites uniformly. The nanowires wrap each other with straight or curved morphology and formed a network. The XRD pattern of the synthesized nanowires is shown in Figure 2(b). The diffraction peaks of the synthesized nanowires at 2\(\theta\)=35.7°, 60.1° and 72.8°C can be observed, which refer to the \(\beta\)-SiC (111), (220) and (311) crystalline planes. The other four peaks marked with C (carbon) refer to C/C substrate. Therefore, the synthesized nanowires are
β-SiC nanowires. The subsequent deposition of SiC in the SiC nanowires resulted in SiC nanowires reinforced SiC coating (SiCNW-SiC). Fig 3(a) shows the XRD pattern of the coating reinforced by SiC nanowires. It indicates the formation of β-SiC in the coating reinforced by SiCNWs. Furthermore, the small peak marked with SF is due to stacking faults. The result of XRD analysis implies that the as-received coating is SiCNWs-SiC. The surface of SiCNW-SiC coating (Figure 3(b)) showed particle packing morphology with small SiC particles. There are no cracks in the SiCNW-SiC coating. The cross-section reveals that the SiCNW-SiC coating has a sandwich structure (Figure 3(c)). The pull-out of SiC nanowires observed in the cross-section (Figure 3(d)) could effectively improve the toughness of SiC coating.
To investigate the thermal shock resistance of the coated C/C samples, the thermal shock tests were performed between 1773 K and room temperature, whose results are shown in Figure 4. It is found that the nanowires could effectively toughen the SiC coating by nanowire pullout, nanowire bridging, micro-crack deflection and good interaction between nanowire and matrix interface. The weight loss of SiCNW-SiC coated C/C composites was 2.38% after 25 times thermal cycling between 1773 K and room temperature, while SiC coated C/C composites was 9.50%. The result of the thermal shock showed that the SiCNW-SiC coating had better thermal shock resistance than SiC coating.

![Figure 4. The thermal cycling curves between 1773 K and room temperature.](image)

**Summary**

SiC coating reinforced by SiC nanowires for Carbon/Carbon composites had been prepared by successive two-step CVD process, during which SiC nanowires porous layer was fabricated firstly and then SiC coating material was infiltrated into it. After introducing SiC nanowires, the SiC coating could effectively reinforced by SiC nanowires.

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**References**