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Enhancement of the oxidation resistance of C/C composites by depositing SiC nanowires onto carbon fibers by electrophoretic deposition

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ABSTRACT

SiC nanowires (SiCNWs) were introduced into carbon fiber (CF) cloth laminated preform by electrophoretic deposition (EPD) and they were used to modify carbon/carbon (C/C) composites. The effects of SiCNWs on the oxidation kinetics and retardation mechanism of C/C composites were investigated. Compared with C/C composites, SiC nanowire reinforced C/C (SiCNW–C/C) composites have a better oxidation resistance since SiCNWs can act as connecting bridges between the adjacent carbon cloth layers, strengthen the adhesion of interlayer matrix, thus inhibit the formation of rapid oxidation channels such as annular matrix cracks and interlamination interface debonding.

1. Introduction

Due to their good thermal and mechanical properties such as high thermal conductivity, low density, high specific strength, good chemical and mechanical ablation resistance, carbon/carbon (C/C) composites have been widely used in aviation and aerospace industries [1–3]. For traditional C/C composites, however, microstructure defects (including matrix annular cracking and degraded fiber/matrix (F/M) interface bonding) were inevitably formed in the preparing process. These defects always acted as oxidation channels and resulted in the drastic degradation of C/C composites, restricting their applications in high-temperature and oxygen-containing environments.

Up to now, in some researches, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been used to modify the C/C composites to maximize the excellent application performance of them. Good results have been obtained such as strengthening the adhesion between pyrocarbon and carbon fibers (CFs) [4], improving thermal conductivity [5], mechanical properties [6–8] and the oxidation resistance [9,10] of C/C composites by introducing CNTs or CNFs. Therefore, introducing the secondary reinforcements with nanostructure is an efficient method to improve the corresponding properties of C/C composites. However, the mostly application environment of C/C composites is in oxygen-containing atmosphere with high-temperature, and the CNTs/CNFs are made up of carbon elements, unable to get rid of the fact that they will be easily oxidized at low temperature in oxygen-containing environment [11]. Therefore, the oxidation resistance of C/C composites modified by CNTs or CNFs is limited.

To improve the oxidation resistance of C/C composites, we wonder whether we can find other substitutions with similar nanostructure but have better antioxidant property to modify C/C composites. As a kind of SiC ceramic, SiC nanowires (SiCNWs) have good oxidation resistance due to the formation of vitreous SiO_2 at high temperature [12]. Owing to their high strength over their bulk-counterparts, SiCNWs have been used as reinforcement material to enhance the strength and toughness of the composites [13,14]. Moreover, SiCNWs have been confirmed to exhibit excellent toughening effects in SiC ceramic matrix composites [15–17]. But so far, little has been reported about the C/C composites modified by SiCNWs, as well as the oxidation resistance of SiC nanowire reinforced C/C (SiCNW–C/C) composites.

SiCNWs can be assembled onto micro-surface of carbon fibers by many methods. Chen et al. [18] reported the synthesis of needle-shaped 3C-SiC nanowires on polyacrylonitrile carbon fibers (CFs) through thermal evaporation, however, the low distribution density of synthesized nanowires leads to low reinforcement efficiency. The composite structure of SiC nanowire and CFs was fabricated by chemical vapor deposition (CVD) process at 1300 °C was also reported by Ref. [19], in which the synthesized nanowires distributing high density and uniformly in the used composite preform. However, the preparation of SiCNW-deposited preform by CVD shows disadvantages of high cost and process complexity

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[17,20]. Furthermore, interfacial reaction between carbon substrates and the raw materials containing Si at high temperature (>1200 °C) in CVD process may damage the structure of CFs [21], which will significantly degrade the mechanical properties of the composites.

In this work, a simple method with mild operating conditions and low-cost, i.e. electrophoretic deposition (EPD) [22–24], was used to prepare SiC nanowire/carbon fiber hybrid reinforcements that were used to fabricate SiCNW–C/C composites. The oxidation resistance of the composites was primarily focused on. Our aim is to improve the oxidation resistance of C/C composites in air and furthermore to evaluate the role of SiCNWs in enhancing the oxidation resistance of C/C composites.

2. Experimental

1 K CF cloths made by T300 polyacrylonitrile-based (PAN) CFs (6–7 μm in diameter, Tianniao, China) and β-SiC nanowires (100–600 nm in diameter, 10–50 μm in length, produced by carbothermal reduction, 99% in purity, Zhuoxi Advanced Material Co. Ltd., China) were used as the starting materials. For electrophoretic deposition, SiCNWs were dispersed in isopropyl alcohol by 2 h ultrasonic to obtain dispersions of 0.5 g/L. CF cloth (40 mm × 60 mm) was fixed in plastic frame by conductive adhesive, and then was immersed in an EPD cell containing stable SiCNWs suspension. A stainless steel plate was placed on opposite side of carbon cloth as counter electrode. The voltage value was 40 V and electrode distance was 15 mm. The deposition time was 40 s, by which CF-based reinforcements deposited with SiCNWs were prepared, containing 2.28 wt% SiCNWs per carbon cloth. The content of SiCNWs deposited on carbon cloth can be calculated by the following equation:

$$m = (m_1 - m_0)/m_0 \tag{1}$$

where m is the mass fraction of SiCNWs deposited on carbon cloth, m_0 is the initial weight of carbon cloth before depositing SiCNWs and m_1 is the weight of the SiCNWs deposited carbon cloth after drying. At least 5 pieces of carbon cloth were weighed and calculated mean value. Sixteen pieces of cloths with SiCNWs were arranged in the same direction and sewed them together using CF tows to form a perform (shown in Fig. 1). For comparison, a perform without SiCNWs was also prepared to make a pure C/C composite. The obtained preforms were then densified in a self-made chemical vapor infiltration (CVI) reactor at 1080 °C at 1 atm using CH_4 (36 L/h) as carbon source and nitrogen (144 L/h) as dilute gas. The density of C/C and SiCNW–C/C composites is 1.63 and 1.64 g/cm^3, respectively. These samples for investigation of oxidation rate have been cut of homogeneous blocks with dimensions about 2 mm × 2 mm × 3 mm. The constant heating rate oxidation behavior and isothermal oxidation behavior of the samples were both studied by thermal gravity test (TGA/DSC1, METTLER TOLEDO, Switzerland) in air. The specimens were heated up from 300 °C to 1000 °C (10 °C/min) under constant heating rate oxidation conditions. The isothermal oxidation tests were carried out at 600, 700, 800 and 900 °C. The samples were heated to the desired temperature in flowing nitrogen (99.99%, 50 ml/min). When the desired temperature was reached, the sample was held at the temperature for about 5 min and then the gas was switched from nitrogen to air. All the specimens were placed in alumina pans and oxidized in a flowing air (50 ml/min). The weight loss during oxidation was monitored as a function of time. The crystalline structure of the SiCNWs was measured with X-ray diffraction (XRD; X'Pert PRO, PANalytical, Almelo, the Netherlands) using Cu Kα radiation ($\lambda = 0.15406$ nm), operating at 35 kV and 20 mA. The morphologies of deposited SiCNWs, the microstructures and the oxidation morphologies of two composites were analyzed by scanning electron microscopy (SEM, MIRA3 XMU, TESCAN) with energy dispersive X-ray spectroscopy (EDS). Polarized light microscope (PLM, Leica DMLP optical microscope) was used to investigate the morphology of pyrocarbon matrix.

3. Results and discussion

Fig. 2 shows the typical SEM images of carbon fibers before and after electrophoretically depositing SiCNWs. As shown in Fig. 2a, the fiber surface was smooth and the striations along the fiber could be seen clearly (Fig. 2a). Fig. 2b shows the morphology of SiCNWs on the surface of carbon fibers. Obviously, when the electrophoretic deposition time is up to 40 s, a porous structure consisting of large amounts of the uniform-distributed SiCNWs with mostly straight morphology can be found on the surface of carbon fibers, the deposition thickness of SiCNWs coating on fibers reaches about 3 μm (Fig. 2c). The diameters of SiCNWs are between 200 and 500 nm, and lengths are a few dozen micrometres. During CVI process, this bulky three-dimensional (3D) network structure formed above the carbon fibers can strengthen the interlamination, which is beneficial to the oxidation resistance ability of composites. Fig. 3 shows the XRD spectrum of the SiC nanowire deposited carbon fiber cloth, which shows a β-SiC structure.

Fig. 4 shows the PLM micrographs of the microstructures of two composites. The matrix pyrocarbons in both composites are smooth laminar (SL) pyrocarbons. In pure C/C composite (Fig. 4a), it can be clearly observed that fibers are primarily surrounded by growth cones and the Maltese cross is smooth, the pyrocarbons have large sizes, few growing characteristics. After introducing SiCNWs, the nucleation active sites for pyrocarbon during CVI increase greatly. Therefore, the pyrocarbon matrix can be refined and then the probability of generating matrix annular cracks caused by thermal stress during fabrication can also be decreased, as shown in Fig. 4b.

To investigate the oxidation resistance ability of two kinds of composites with and without depositing SiCNWs, the constant heating rate oxidation test was characterized by TGA from 300 °C to 1000 °C in air. The results are shown in Fig. 5. It is clear that the weight loss of two composites increases rapidly with increasing temperature due to the readily oxidation nature of the carbon material. From the curves we can see that the C/C composite has a 56% percentage weight loss after oxidation. While the SiCNW–C/C composite has a better oxidation resistance and its weight loss percentages is 51%. Moreover, the oxidation starting temperature of C/C composite and SiCNW–C/C composite are 500 °C and 590 °C, respectively. Compared to C/C composite at the same oxidation process, SiCNW–C/C composite exhibit a slower rate of oxidation weight loss and higher oxidation starting temperature, indicating adding SiCNWs can prolong the oxidation.

Fig. 6 shows the isothermal oxidation curves of C/C and SiCNW–C/C composites at different temperature. The curves of both composites are similar which indicates the same oxidation mechanism of two composites. It can be seen that the weight loss is a linear function of time at 0–60% weight loss and obviously non-linear over 60% under four oxidation temperatures. At 600 °C, both composites are slowly oxidized. After oxidation for 200 min, the weight

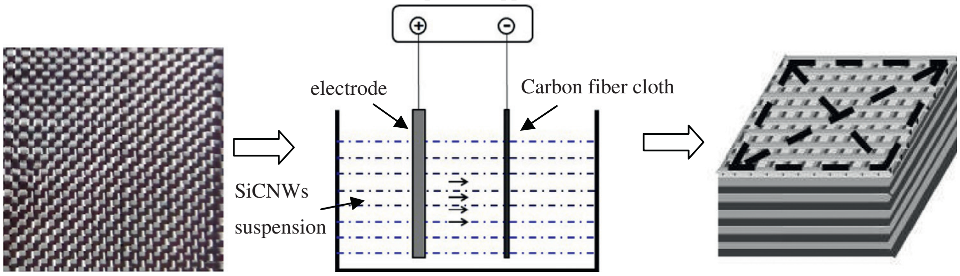

Fig. 1. Schematic diagram of CF cloth laminated perform.