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In-situ synthesis silicon nitride nanowires in carbon fiber felts and their effect on the mechanical properties of carbon/carbon composites

Jinhua Lu *, Kebing Guo, Qiang Song *, Yunyu Li, Leilei Zhang, Hejun Li

State Key Laboratory of Solidification Processing, Carbon/Carbon Composites Research Center, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

Si_3N_4 nanowires (Si_3N_4NWs) were in-situ synthesized in carbon fiber felts via catalyst-assisted pyrolysis of polyureasilazane and further to be used to reinforce carbon/carbon (C/C) composites. Effects of ferrocene-to-acetone mass ratio and synthesis temperature on the morphologies of Si_3N_4 products were investigated and their optimized values are 2:98 and 1430 °C respectively. When the ferrocene-to-acetone mass ratio is 2:98 and the temperature exceeds 1500 °C, a great number of disorganized ribbon-like products were obtained. The growth of Si_3N_4NWs or ribbons obeys a solid-liquid-gas-solid (SLGS) mechanism. Si_3N_4NWs can improve the mechanical properties of C/C composites obviously. Compared with the pure C/C specimens, the specimens doped with Si_3N_4NWs have 66.7% and 58% improvements in out-of-plane compressive and interlaminar shear strength, which can be further increased to 166.7% and 65% through coating a layer of pyrolytic carbon on carbon fibers before the immersing of PSN. These improvements are attributed to the formation of three-dimensional interlocked carbon matrix and the enhanced bonding between pyrolytic carbon plies induced by Si_3N_4NWs.

1. Introduction

C/C composites have been widely used in aerospace applications due to their unique and superior properties such as light weight, low coefficient of thermal expansion, high thermal conductivity, good thermal-shock resistance and ablation resistance [1–2]. However, 2D C/C composites, as one of the widely used C/C composites, have great deficiency in out-of-plane compressive strength and interlaminar sheer strength due to the pyrolytic carbon with poor mechanical property and the matrix annular crack, which limit their wide application to load bearing part [3–4]. In order to deal with this problem, introducing some high-strength ceramic nanowires or carbon nanotubes into carbon fiber felt preforms to promote the strength of 2D C/C composites at micron and nanometer scales has received extensively concern [5–11].

Silicon nitride (Si_3N_4) is a kind of high-strength structural and functional ceramic material. Si_3N_4 nanowires, as one of the most important one-dimensional nanostructures, have some excellent physical and chemical properties, such as good surface appearance, low coefficient of thermal expansion, high mechanical strength, remarkable thermal and chemical stability and tunable optoelectronic properties [12–15]. These superior properties make Si_3N_4 nanowires a promising candidate for the matrix enhancement of C/C composites. Though several methods have been reported to synthesize Si_3N_4 nanowires on the surface of matrix [12,16–20], the method of in-situ synthesis Si_3N_4 nanowires in carbon fiber felt preforms has not been researched and the mechanical properties of Si_3N_4 nanowires reinforced 2D C/C composites have not been studied either.

In this work, the catalyst content and growth temperature to synthesize Si_3N_4 nanowires in carbon fiber felt via pyrolysis of polyureasilazane (PSN) are detailedly studied in order to achieve the optimized parameters. Then the carbon fiber felt preforms doped with Si_3N_4 nanowires were densified by isothermal chemical vapor infiltration (ICVI). The out-of-plane compressive and interlaminar shear behaviors of the Si_3N_4 nanowires reinforced C/C composites (Si_3N_4NWs-C/C) were tested and the strengthening mechanisms of Si_3N_4 nanowires to 2D C/C composites were discussed in detail [7,21].

2. Experimental procedure

2.1. Synthesizing Si_3N_4 nanowires in carbon fiber felts

Bulk density and fiber diameter of the carbon fiber felts used in this work were 0.2 g/cm^3 and 7–9 μm, respectively. The method to synthesize Si_3N_4 nanowires in carbon fiber felts was catalyst-assisted pyrolysis of polymeric precursors. Hence, polyureasilazane (PSN) (Institute of Chemical, Chinese Academy of Science, Beijing, China), acetone, and ferrocene were adopted as the starting materials. PSN was diluted with acetone about 15 times, then the solution was uniformly mixed by a magnetic stirrer for 1 h. Carbon fiber felts with the dimension of 60 mm × 35 mm × 10 mm were immerged into the above solution for 5 min, then dried in the drying oven for 10 h at 70 °C. After that, the preforms were immerged into the suspension of ferrocene and acetone

* Corresponding authors.
E-mail addresses: lujinhua@nwpu.edu.cn (J. Lu), plusring@163.com (Q. Song).

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(the mass ratios of the ferrocene to acetone are 1:99, 2:98 and 3:97) for 5 min, then dried in air.

Heat treatment process was carried out in a horizontal tube furnace under the protection of ultra-high purity nitrogen with the flow rates 100 sccm (standard cubic centimeters per minute). The felts were firstly heated to 260 °C, and kept in this temperature for 2 h. Then the temperature was raised to 1400–1550 °C at 10 °C/min, and hold for 2 h. In the end, the system was naturally cooled down to room temperature.

2.2. Fabrication and mechanical tests of the specimens

The optimized parameters were used to synthesis Si_3N_4 nanowires in carbon fiber felts. All the felts were densified by isothermal chemical vapor infiltration (ICVI) at 1080 °C using CH_4 as the precursors to fabricate C/C composites. For comparison, three groups of composite specimens were prepared (labeled by C/C, Si_3N_4NWs-C/C and Si_3N_4NWs-C-C/C composites, respectively). Both Si_3N_4NWs-C/C and Si_3N_4NWs-C-C/C were doped with Si_3N_4 nanowires. However, the main difference between them is that only the preforms of Si_3N_4NWs-C-C/C were coated with a layer of pyrolytic carbon (several dozens of nanometers) by CVI before synthesizing Si_3N_4 nanowires. The final density of the whole specimens is about 1.62 ± 0.02 g/cm^3.

2.3. Characterization methods

The distribution and morphologies of Si_3N_4 products in carbon fiber felts and the fracture morphologies of composite specimens were characterized using scanning electron microscope (SEM, FEI NANOSEM 450). The microstructures and phases of Si_3N_4 nanowires were characterized by high-resolution TEM (HRTEM, FEI TECNAI G20) with energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD, Philips X'Pert PRO, Cu Kα radiation, 0.15406 nm). Out-of-plane compressive and interlaminar shear properties of the three groups of specimens were tested on an electronic universal testing machine (CMT 5304, Suns Co. China). Five specimens were done for each test.

3. Results and discussion

3.1. In-situ synthesis Si_3N_4 nanowires in carbon fiber felts

Catalyst is an important factor for the synthesis of Si_3N_4 nanowires in carbon fiber felts via pyrolysis of polymeric precursors [12,17]. In this work, the preparation temperature was set as 1430 °C. Fig. 1 distinctly shows that, with the increase of ferrocene-to-acetone mass ratio, the morphologies of obtained products in carbon fiber felts change a lot. When the ferrocene-to-acetone mass ratio is 1:99 (Fig. 1a and inset), a great number of residual Si-C-N ceramic pieces were observed in felt; meanwhile, only a small number of agglomerate nanowires existed in the space between fibers, which indicates that the Si-C-N ceramic cannot convert into Si_3N_4 nanowires sufficiently at low catalyst loading. The high-resolution SEM image of single nanowire, which is showed in Fig. 1a, indicates the absence of catalyst droplet on its top. When the ferrocene-to-acetone mass ratio increases to 2:98 (Fig. 1b and inset), Si-C-N ceramic pieces cannot be found. The synthesized Si_3N_4 nanowires with moderate diameter (about 50–100 nm) and length (about 20–50 μm) are uniformly distributed in the felt and interweave small network between carbon fibers. When ferrocene-to-acetone mass ratio is 3:97 (Fig. 1c and inset), the products become thicker and longer, and are randomly distributed with serious agglomeration in the felt. The inset images of Fig. 1c show the detailed morphologies of single wire's top and root; similar catalyst particles cannot be found either on the top or on the root. The EDS patterns (Fig. 1d) of point A and point B also show the absence of Fe element. Carbon element is detected at point B, which may come from the product during reaction. In addition, metal catalyst particles can dissolve into carbon fibers and weaken their outer layers at the reaction temperature above 723 °C, leading to fiber strength failure [26]. Thus the concentration of catalyst should be limited, indicating that the 2:98 ferrocene-to-acetone mass ratio is optimized to synthesize Si_3N_4 nanowires.

In order to study the effect of preparation temperature on nanowire growth [22], a series of varied temperature experiments were carried out at the constant ferrocene-to-acetone mass ratio (2:98). Fig. 2

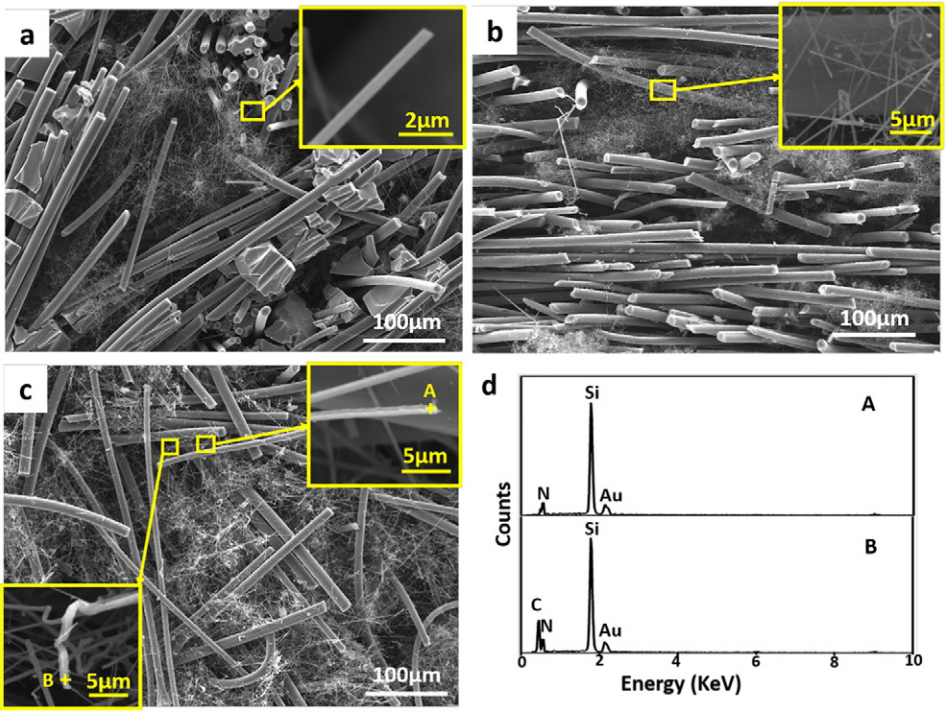

Fig. 1. SEM images of the products synthesized in carbon fiber felts at 1430 °C, at the ferrocene-to-acetone mass ratio of 1:99 (a and inset), 2:98 (b and inset) and 3:97 (c and d), and the EDS pattern of point A and point B (d).