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Oxidation behavior of Si_3N_4 fibers derived from polycarbosilane

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ABSTRACT

Si_3N_4 fibers prepared from polycarbosliane are exposed in dry and wet air respectively from 800 to 1300 °C for up to 1 h. After dry air oxidation, an uniform SiO_2 coating doped with nitrogen is formed on fiber surface. However, the coating obtained in wet air is much thicker with more complex microstructure containing sub-layers of N-doped SiO_2, near stoichiometric Si_3N_4 and graphite-like nanoribbons. Activation energy for oxidation in wet and dry air is determined as 108 and 152 kJ mol^{-1}, respectively. Both of the values are lower than the known Si_3N_4 materials with E_a of 259–485 kJ mol^{-1}.

1. Introduction

Continuous silicon nitride (Si_3N_4) thin fiber is a family of polymer-derived ceramic fibers composed of Si and N, and is commonly doped with different amount of C and O according to the precursor structures [1–4] and preparation techniques [5–7]. The non-stoichiometric nature of the precursor results in uniformly disordered structures in the fiber after pyrolysis. Consequently, most of the polymer derived Si_3N_4 fibers are amorphous up to 1400 °C and retain high tensile strength [8–11]. With additional characters of high electrical resistivity, low thermal conductivity and low dielectric constant, the continuous Si_3N_4 fibers are promising reinforcements for thermal insulation and microwave-transparent composites [12–14]. In recent years, one of the expected applications of Si_3N_4 fibers has been indicated as reinforcement in the high temperature microwave-transparent composites as replacement of the SiO_2 fiber, which losses most of its original strength when serving at above 900 °C, owing to the severe grain coarsening [15–17]. Nevertheless, also the Si_3N_4 fibers face challenges during service in air, because of passive oxidation of the fiber surface and microcracking at the fiber/oxidation coating interface.

To date, studies on the oxidation behavior of Si_3N_4 were conducted mainly on powders and bulks [18–25]. Results indicated that the oxidation rates of Si_3N_4 depended upon the purity of the material. The lowest oxidation rates were observed for high-purity chemical vapor deposited (CVD) Si_3N_4 [25]. However, these works contributed little to knowing the oxidation behavior of the continuous Si_3N_4 fibers, which was not only because of the variations in composition between bulks and fibers, but also due to the particularity of the fibers with respected to heat transfer process and the resultant structural characters. Studies regarding the Si_3N_4 fibers mainly dealt with the crystalline behavior of the fibers at high temperatures in inert atmospheres. Matsuo et al. studied the structural evolution of perhydropolysilazane (PHPS)-derived Si_3N_4 fiber after heating at 1400–1500 °C in N_2. α-Si_3N_4 particles were only detected on the fiber surface, which seemed to be proceeded by a vapor phase growth mechanism [26]. Gilkes et al. explored the microstructure of hydridopolysilazane (HPZ)-derived Si_3N_4 fibers by using neutron scattering and nuclear magnetic resonance [27]. The HPZ-Si_3N_4 fibers were found to contain excess crystalline silicon and disordered carbon, and the fibers annealed in N_2 at 1400 °C for 100 h contained a cristobalite phase. Similar results evidenced that these polymer-derived Si_3N_4 fibers had excellent thermal stability [28]. Cinibulk et al. investigated the oxidized microstructure of a Si-B-C-N-based fiber derived from an *N*-methylpolyborosilazane precursor. With presence of B, complicated coating structure formed on the fiber surface upon heating in stagnant laboratory air at 1500 °C for 2 h. Although the fiber core retained its amorphous nature, the fiber suffered significant strength degradation after oxidation [29].

In the present work, Si_3N_4 fiber derived from polycarbosilane (PCS) are exposed to wet and dry air respectively in a temperature range from 800 to 1300 °C for up to 1 h. Microstructure, mechanical property and oxidation kinetics of the oxidized Si_3N_4 fiber are explored. The effect of reactive gas species on oxidation behavior of the Si_3N_4 fiber is here discussed.

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Table 1
Chemical composition of the as prepared Si_3N_4 fibers.

Element	Si	N	O	C
Concentration (wt.%)	71.06	27.47	0.57	0.90

2. Experimental procedure

The PCS precursor is synthesized following the Yajima's route [30,31]. The average molecular weight (M) is 1190, and the softening point is 189 °C. The obtained PCS is used as precursor of the Si_3N_4 fiber and treated through the route developed by Japan atomic energy research institute [7]. Table 1 shows the chemical composition of the as-prepared Si_3N_4 fibers. Average tensile strength of the fiber is 936 ± 87 MPa.

For oxidation experiment, green fibers are placed in alumina crucible and pushed into alumina tube furnace with $MoSi_2$ as heating element. Wet air is obtained by blowing compressed dry air (Linde Gas, 99.99%, China) into deionized water in an airtight container, which was connected directly to the furnace tube. Partial pressure of the water vapor can be controlled by changing the dry air pressure as well as the water temperature according to Ideal Gas Law. In this work, the partial pressure of water vapor is 2.4 KPa. The heating rate of the oxidation is 5 °C min^{-1}. The holding times at each target temperature, 800, 1000 and 1300 °C, are 0.5 h and 1 h respectively. Tensile strength of the single fiber is tested at room temperature using an electronic single fiber strength tester (SLBL-10N, SHIMADZU, Japan). 25 specimens are used in each test. The gauge length is 25 mm and the loading rate is 1 mm min^{-1}.

The phases of the fibers are identified using an X-ray diffractometer (D8 Advance, Bruker-AXS, Germany). The microstructure is characterized using SEM of 30 keV (SU-70, Hitachi, Japan) and by TEM of 200keV(JEM 2100, JEOL, Japan and Talos F200S, FEI, USA). The TEM specimens are prepared by a special embedding method reported elsewhere [32]. The embedded specimens are thinned by cutting, mechanical grinding, dimpling and ion milling.

3. Result and discussion

3.1. Microstructural evolution of the Si_3N_4 fiber after oxidation

Fig. 1 shows the weight changes of the Si_3N_4 fibers after oxidation. All of the treated fibers gain weight. The weight gain in wet air is significantly higher than that in dry air, indicating that the oxidation reaction is promoted by wet air condition. Similar results were also obtained in the oxidation of crystalline Si_3N_4 and SiC materials

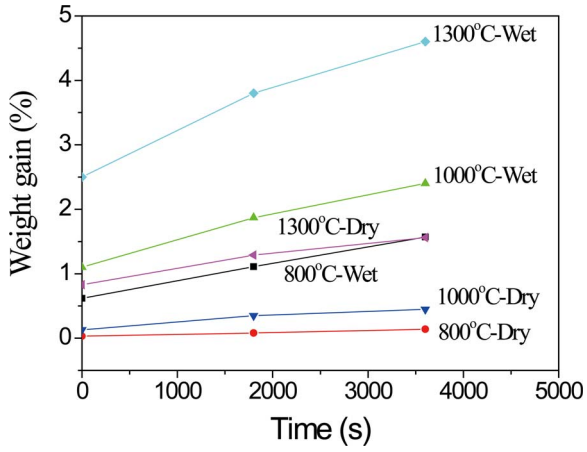

Fig. 1. Weight gain of Si_3N_4 fibers after oxidized in (a) wet air and (b) dry air.

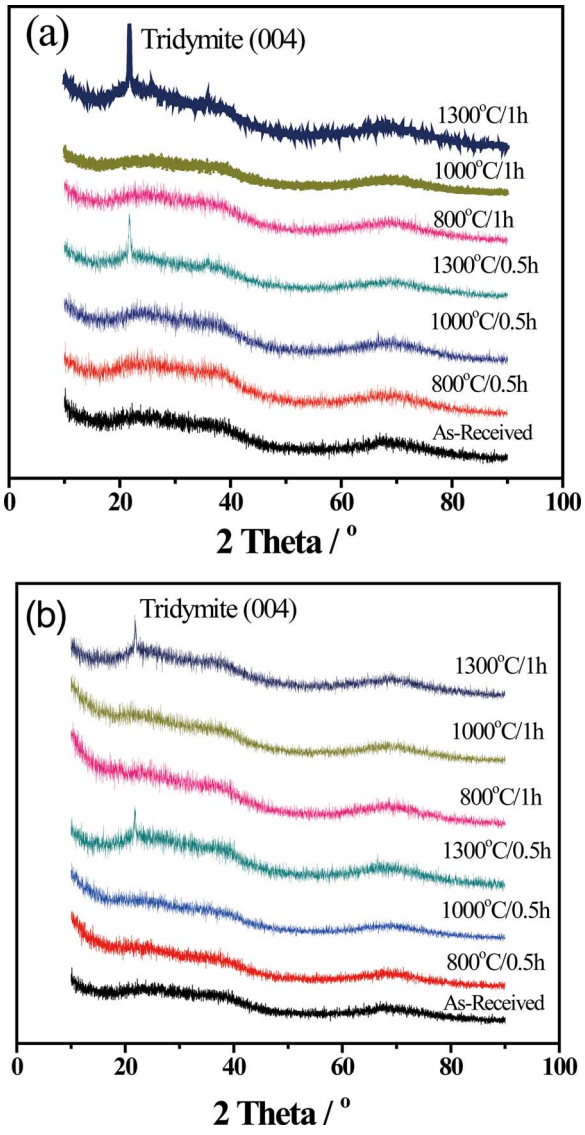

Fig. 2. X-ray diffraction patterns of the Si_3N_4 fibers after oxidized in (a) wet air and (b) dry air.

[33–35]. Whether in wet or dry air, the weight of the oxidized fibers increases with increasing temperature. As the Si_3N_4 fibers are oxidized at 800 °C, the weight gain in isothermal processes changes almost linearly with the soaking time, indicating the oxidation process is controlled by surface reaction. However, above 1000 °C, the weight gain in last half hour becomes lower than that in first half hour. This indicates that the oxidation is retarded at high temperatures, since the inward diffusion of oxidizing gases is restricted and becomes a rate-controlling process as the thickness of the oxidated coating increases.

Fig. 2 shows the XRD pattern of the treated Si_3N_4 fibers. All the Si_3N_4 fibers remain amorphous even after oxidation at 1300 °C for 1 h. The sharp peak at 21.8° after heating at 1300 °C belongs to lattice plane (004) of tridymite, which results from the crystallization of the silica coating. Based on the Scherrer formula, grain size of the tridymite coatings obtained after different treatments can be estimiated by the change of the FWHM (Full width at half maximum of peak intensity). As compared with the dry air oxidation, the Si_3N_4 fiber oxidized in wet air at 1300 °C/1 h has a (004) peak of higher intensity with narrower FWHM (~70% width of the FWHM obtained in dry air), indicating a larger grain size of the tridymite and a higher crytallinity degree of the coating. Results suggest that water vapor promotes not only the oxidation reaction, but also grain growth of SiO_2.