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Characterization and properties of silicon carbide fibers with self-standing membrane structure

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ABSTRACT

SiC fibers with self-standing membrane structure in large scale are prepared by one-step thermal reduction method by using carbon black and gangue as raw material at 1500 °C for 2 h in argon. The average pore size of the membrane is 1.603 μm using the bubble-point method. The synthesized SiC fibers are well-developed cubic structure with the diameter in the range of 100–500 nm and length up to several millimeters. In addition, SiC fibers possess good oxidation resistance up to 1250 °C in air and low thermal expansion coefficient of 4.385–4.655 × 10^{-6}/°C from room temperature to 750 °C. The oxidation behavior of SiC fibers depends on temperature and sample shape. Based on this, the oxidation kinetics is dealt with the real physical picture (RPP) model and gets a good agreement with the experimental data.

1. Introduction

Ceramic fibers as a kind of fibrous lightweight material have drawn a significant amount of attention because of its excellent physical and chemical properties [1]. Among them, silicon carbide (SiC) fiber is characterized by high strength, corrosion resistance, good refractory and low density etc. [2,3]. Therefore it is extensively applied in the fields of diesel engines, aerospace, thermal conductor and fusion reactors etc. [3–10] as the key component in reinforced ceramic matrix composites (CMCs) under harsh working conditions. Considering its enormous potential application, much effort has been spent on synthesis and characterization of SiC fibers over the past decades. As for the fabrication techniques, various methods including chemical vapor phase growth deposition (CVD) [11–13], electron beam irradiation curing (EBIC) [14–16], electrospinning (ES) [17], polymer impregnation pyrolysis (PIP) [18–22], catalyst-assisted pyrolysis of polysilazane precursor (CAP) [23–30] and silicon gel carbon thermal reduction (SGCTR) [31,32] etc. have been reported and got some success in industrial production. However the methods of CVD and EBIC require strict condition and thus are at high costs. ES, PIP and PSN methods are characterized with complex process and superior cost because they are prepared from specific precursors. Besides, SGCTR method is difficult to obtain uniform morphology. Therefore it's desirable to propose a new method to prepare SiC fibers efficiently and economically.

As for the properties of SiC fibers especially at high temperature, Takeda et al. [20] investigated the oxidation behavior of polycarbosilane-derived SiC fibers at 1000–1400 °C in air for 1–100 h. The result showed that the fibrous structure maintained well except that some pores and fractures appeared. Bunsell et al. [33] pointed out that there still much work remained to be done to keep the fiber stable above 1000 °C. Besides these, there is no further work to be carried out on the high temperature properties of SiC fibers. This brings a lot of difficulty for the application of materials, for instance, CMCs reinforced by SiC fibers.

Herein one-step carbon thermal reduction method was adopted to synthesize SiC fibers with uniform morphology using the raw materials of carbon black and the gangue. By controlling the atmosphere and temperature, large amount of SiC fibers with self-standing membrane structure was prepared. Considering the application of SiC fibers under harsh conditions, the high temperature properties of SiC fibers including the oxidation behavior up to 1450 °C in air and the thermal expansion coefficient from room temperature to 750 °C were also investigated.

Compared with SiC nanofibers/nanowires by using the thermal reduction of SiO_2 and active carbon reported in the

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literature [34–40], the difference and advantage of our work are following: (1) In view of the synthesis condition, the reaction temperature and the ratio of gangue and carbon black are selected at a reasonable range in this work. This can avoid both the removal of the residual carbon [34,35] and too high reaction temperature [36]. (2) As for SiC fibers produced in this work, the synthesized SiC fibers are well-developed cubic structure with high purity and uniform morphology. The stacking defect (SF) of SiC fibers is relatively less than the reported result in the literature [37–40]. What's more, the synthesized product is self-assembled into membrane structure, showing its potential application as filter. (3) As for the properties of SiC fibers, less work about the thermal property of SiC fibers is reported. In this work, the properties of SiC fibers including oxidation resistance and thermal stability are investigated. These fundamental data may pave the way for the application of SiC fibers at high temperature.

2. Material and methods

2.1. Material preparation

Gangue (SiO_2 > 99%) and carbon black were used as silicon and carbon sources respectively. The powder with the mole ratio of 1:3 (SiO_2/C) was ball mixed. Preparation of SiC fibers was mainly taken place in a high temperature furnace using carbon as the inner lining, which is described in detail in our recent work [41]. During the whole process, argon with the purity of 99.9% at the rate of 0.4 L/min was adopted as protecting atmosphere and the total pressure was kept at 0.1 MPa. When the furnace was cooled naturally to room temperature, argon was stopped and gray–white self-standing membrane in large scale was obtained mainly on the top of the furnace. The resulting fibers were washed with 10% hydrofluoric acid (HF) for 1 h to remove the remained silica.

2.2. Phase and microstructure characterization

The phase was characterized using a 21 kW extra-power powder X-ray diffractometer (XRD) (M21XVHF22, Mac Science Co. Ltd., Yokohama, Japan) with Cu Kα (λ = 1.54056 Å) radiation over a 2θ range from 10 to 90°. The morphology and microstructure of the synthesized fibers were observed using a scanning electron microscopy (SEM: Model JSM-840A, JEOL, Tokyo, Japan) and transmission electron microscopy with SAED (TEM: Model Tecnai G2 F30 S-TWIN, FEI, America). The pore size of the fibrous membrane was investigated by a capillary flow porometer (IB-FT Germany, POROLUX 1000) based on bubble-point method [42,43].

2.3. High properties of SiC fibers

The thermal expansion coefficient of SiC fibers was determined using an advanced analyzer (SETARAM Setsys Evo TMA). The experiments were carried out in an accurate dilatometric cycle running measurements at the heating rate of 10 °C/min from room temperature to 750 °C and then cooled to room temperature as a cycle at nitrogen atmosphere. In the experiment, the sample was pressed into the cylinder with 10 mm in diameter and 3 mm in height. The linear thermal expansion coefficient was calculated from the following equation:

$$\rho = \frac{L_T - L_0 + Ak(T)}{L_0} \quad (1)$$

where ρ is the linear thermal expansion coefficient (/°C). L_0 (mm) and L_T (mm) are the length of the sample at room temperature and the experimental temperature T, respectively. Ak(T) (mm) is the correction value of the instrument at the experimental temperature T.

The oxidation behavior of SiC fibers was investigated under both non-isothermal and isothermal conditions using a thermoanalyzer (Netzsch STA 449C, Netzsch, Germany). The TG microbalance had the sensitivity of 1 mg. Before isothermal oxidation experiments, non-isothermal oxidation from 600 to 1500 °C at the heating rate of 10 °C/min in air was investigated to have knowledge of the oxidation behavior of SiC fibrous membrane. In the isothermal experiments, SiC fibers (about 7.1 mg) were placed in an alumina crucible and the temperature was rapidly raised to the required level in a flowing purified argon gas. After the thermal equilibrium was established, argon was stopped and air was then introduced. The mass change due to oxidation was then monitored continuously for 2 h at the rate of 2 point/min. In all the experiments, the flow rate of air was kept constant, i.e. 40 ml/min. To ensure the data to be as accurate as possible, every experiment was repeated at least three times and got the average value.

3. Results and discussion

3.1. Phase and microstructure characterization

Fig. 1 is the optical image of the synthesized product. It can be seen that it is self-assembled into membrane structure. The cross section of the membrane is consisted of SiC fibers as shown in the inset of Fig. 1. The XRD pattern as shown in Fig. 2 is indexed from left to right as (111), (200), (220) and (311) corresponding to 3C–SiC (Card No.104 01-073-1665), indicating that SiC with high purity is obtained. Traditionally, SF are frequently found in 3C–SiC [44], whose density can be measured by SF peak (about 33.6°) be divided by (200) peak (41.4°). In this work the SF peak almost disappeared and (200) peak was also very weak, indicating that the density of SF in the synthesized SiC fibers was relatively less.

Fig. 3a and b shows SEM images of the overall look of SiC at low magnification. It can be seen SiC fibers are uniform. At high magnification (Fig. 3c), SiC fibers are long and straight filaments with diameter between 100 and 500 nm and length up to several millimeters. In addition, the straight fibers possess a smooth surface. There are also some SiC fibers with the bamboo-like morphology (Fig. 3d). A large number of SEM examinations have been carried out. The bamboo-like whiskers account for 5% or so of the total fibers using statistical method.

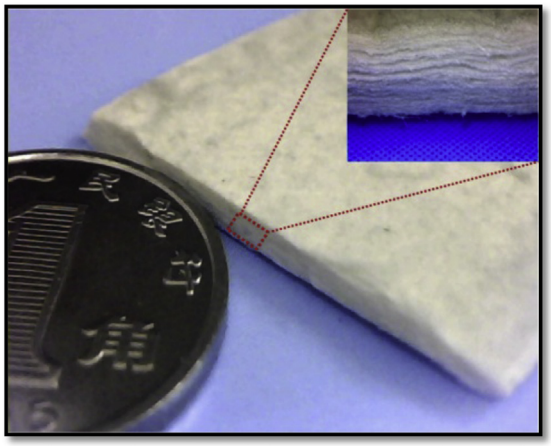

Fig. 1. Optical image of the synthesized SiC fibers and the inset of cross section at high magnification.