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Preparation and properties of hexagonal boron nitride fibers used as high temperature membrane filter

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ABSTRACT

Hexagonal boron nitride fibers were synthesized via polymeric precursor method using boric acid (H_3BO_3) and melamine ($C_3H_6N_6$) as raw materials. The precursor fibers were synthesized by water bath and BN fibers were prepared from the precursor at 1873 K for 3 h in flowing nitrogen atmosphere. The crystalline phase and microstructures of BN fibers were examined by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and high resolution electron microscopy. The results showed that h-BN fibers with uniform morphology were successfully fabricated. The well-synthesized BN fibers were polycrystalline with 0.4–1.5 μm in diameter and 200–500 μm in length. The as-prepared samples exhibited good oxidation resistance and low thermal expansion coefficient at high temperature.

1. Introduction

Boron nitride (BN) is a structural analog of carbon, existing in rhombohedral (r-BN), hexagonal (h-BN) [1], cubic (c-BN), turbostratic and amorphous forms [2]. In a hexagonal structure, the interlayer interactions are weak (van der Waals type) and the interalayer are strong covalent B–N bonds (sp^2), as in the graphite structure. Based on the structural similarities between h-BN and graphite, h-BN is expected to form nanofiber and nanotube structures as an important material applied in many advanced fields due to its unique properties such as lower dielectric constant, higher thermal conductivity, higher temperature stability and strength, higher corrosion and oxidation resistance than carbon [3,4]. Recently the fibrous membranes has arisen great interest of researchers because of their unique advantages, i.e. high porosity, large surface area per unit volume and interconnected open pore structure [5,6]. These characteristics together with the excellent properties of h-BN [4,5] make it attractive for filtration applications, especially used as high temperature membrane filters.

Compared with some 1D nanomaterials, such as cabon nanotube [7,8], oxide nanowires [9,10] and polymer nanowires [11] which have been widely investigated, the research and application of BN fibers lags far behind mainly due to the shortage of a simple and efficient synthetic method. BN nanotubes have been prepared by arc-discharge technique [12], laser heating of h-BN at high nitrogen pressures [13], thermal annealing of amorphous boron powder under lithium vapor in h-BN crucible [14] and CVD from borazine using NiB powders as a catalyst etc. [15–17]. Among these methods, complicated and expensive apparatus or severe preparation conditions are required, resulting in the small amount production. Some researchers introduce a new method to synthesize continuous BN nanofibers by solution coating electrospun template fibers [18,19] or through the polymer-derived ceramics route [5,20–22]. However, the procedure is too complicate and difficult to reproduce the experimental results. In addition, synthesis of BN fibers by electrospinning or the polymer-derived ceramics route is still a challenge due to lack of appropriate precursors and the complexity of the thermal conversion process. Therefore, a new simple and efficient synthesis method to prepare BN fibers has been highly desired.

Herein we developed a simple and innovative method to prepare h-BN fibers with uniform morphology using boric acid (H_3BO_3) melamine ($C_3N_6H_6$) as raw materials. This kind of method has also been adopted by other researcher to prepare BN nanostructure used in cosmetics [23]. In our work, h-BN fibers were prepared. Besides this, the high temperature properties such as oxidation resistance and thermal expansion of BN fibers were investigated considering the possible application of BN fibers as hot-gas filters.

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2. Experimental

2.1. Synthesis of h-BN fibers

Preparation of h-BN fibers includes two steps, i.e. (1) Synthesis of the precursor fibers using H_3BO_3 (≥99.8 mass%) and $C_3N_6H_6$ (≥99 mass%) as raw materials; (2) Conversion of the precursor fibers into BN fibers at 1873 K in flowing nitrogen atmosphere. The precursor fibers were prepared using wet chemical method. A solution containing H_3BO_3 and $C_3N_6H_6$ with the molar ratio of 3:1 was stirred for about 30 min at 363 K to ensure the two powders to be mixed uniformly and reacted completely. The mixture was held for about 12 h at room temperature and was then filtrated by pumping and dried to obtain the white fibers as the polymer precursor. The obtained precursor was then slowly heated in a vertical furnace to 1873 K for 3 h in flowing nitrogen atmosphere. When the furnace was cooled naturally to 573 K, nitrogen was stopped and the white fibers were obtained. The preparation procedure in detail has been reported in our recent work [24].

2.2. 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 100°. The surface morphology of the synthesized fibers was observed by a field emission scanning electron microscopy (FE-SEM) (Supra 55, Zeiss Co., Germany) and transmission electron microscopy (TEM, HITACHI H8100, Hitachi, Japan). High resolution electron microscopy (HRTEM, JEM 2010, Joel Ltd. Japan) operating at 200 kV was used to characterize the phase and crystal morphology of the products.

2.3. High temperature properties

The oxidation behavior of BN fibers was examined on a thermoanalyzer (Netzsch STA 499c, Netzsch, Germany) at the heating rate of 20 K/min from room temperature to 1423 K in flowing air atmosphere. The thermal expansion coefficient of h-BN 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 K/min from room temperature to 873 K and then cooled to room temperature as a cycle in 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 through the following equation:

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

where ρ is the linear thermal expansion coefficient (/K). 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.

3. Results and discussion

3.1. Phase and microstructure characterization

The XRD pattern of the prepared BN fibers is shown in Fig. 1 and is highly ordered as h-BN with lines indexed from left to right as (0 0 2), (1 0 0), (1 0 1), (0 0 4), (1 1 0) and (1 1 2) (JCPDS card No. 34-0421) [25]. Fig. 2a and b shows the morphology of the synthesized h-BN fibers. It can be seen that the morphology of h-BN is fibers-like and uniform with about 0.4–1.5 μm in diameter and 200–500 μm in length.

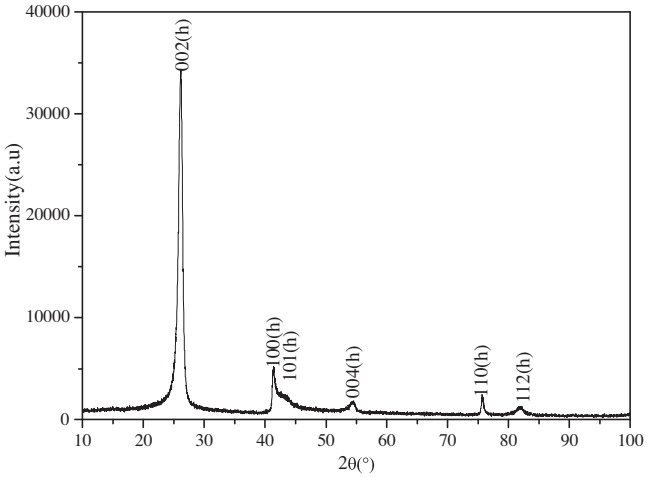

Fig. 1. XRD pattern of h-BN fibers.

TEM micrograph of h-BN fibers together with the results of the selected area electron diffraction (SAED) and HRTEM is shown in Fig. 3. The diameter of h-BN fibers was about 0.5 μm. The diffraction patterns (Fig. 3b) and HRTEM (Fig. 3c) indicate that the synthesized BN fibers are polycrystalline.

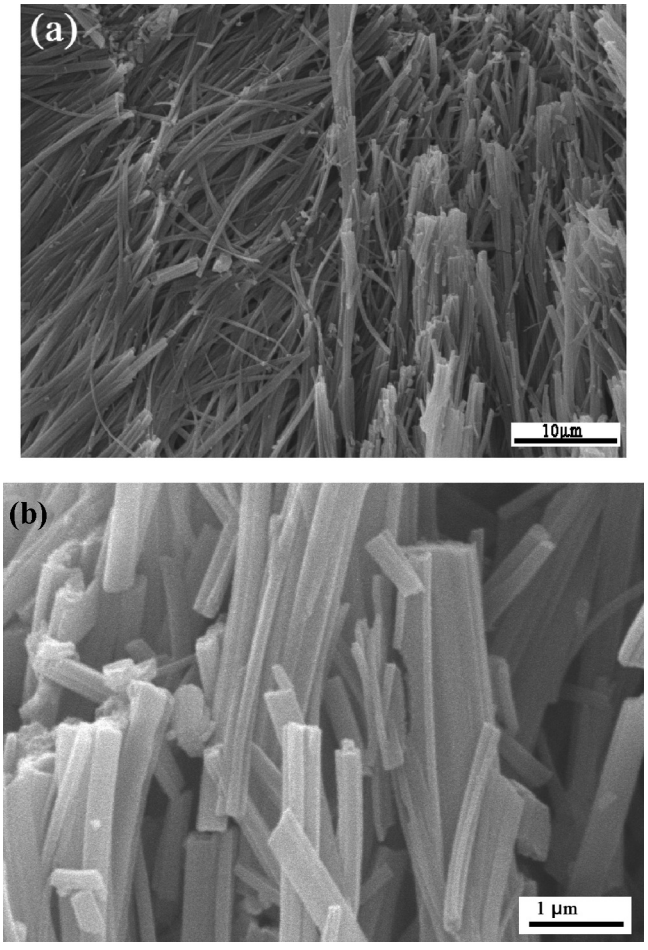

Fig. 2. SEM photo of h-BN fibers.