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Facile synthesis of hexagonal boron nitride fibers with uniform morphology

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Abstract

Hexagonal boron nitride (h-BN) fibers were synthesized via the polymeric precursor method using boric acid (H_3BO_3) and melamine ($C_3H_6N_6$) as raw materials. The precursor fibers were synthesized by a water bath and BN fibers were prepared from the precursor at 1600 °C for 3 h in flowing nitrogen atmosphere. The products were characterized by X-ray powder diffraction, Fourier transformation infrared spectroscopy, thermogravimetry and scanning electron microscopy. The results showed that h-BN fibers with uniform morphology were successfully fabricated. The well-synthesized fibers were 1–2 μm in diameter and 200–500 μm in length.

Keywords: B. BN fibers; Microstructure; Uniform morphology

1. Introduction

Boron nitride (BN) is well known for its excellent properties such as extremely high hardness, high temperature stability, high electric insulation, low dielectric constant and so forth [1,2]. These unique properties make BN a promising material for many applications such as refractories, lubricants, electrical insulators, laser devices and catalyst supports [2–5].

Till now, intensive research works have been carried out on the synthesis of BN, especially h-BN, which possesses hexagonal structure with properties' similar to those of graphite. Some works have been carried out to synthesize BN by a high temperature synthesis routes, carbothermal reduction of boric oxide and direct nitriding of boric acid with ammonia gas, etc. [6,7]. Besides these methods, other methods were also developed to prepare BN. For example, Narula et al. [8] and Kimura et al. [9] synthesized BN by preceramic method using poly(borazinylamine) as the precursor. Rao and Kaner [10] and Solozhenko et al. [11] reported a self-propagation route to synthesize crystalline BN powder using MBF_4 (M—K or Na), Li_3N and NaN_3. Recently, BN was reported to be prepared at very low temperature [12,13]. Hu et al. [14] reported that nanocrystalline BN with the whisker-like morphologies could be synthesized through the reaction of KBH_4 and NH_4Cl at 650 °C. Chen et al. [15] synthesized BN with whisker-like and flake-like morphologies through the reaction of BBr_3 and Mg_3N_2 at 400 °C.

Like many other non-oxide ceramics, the application of h-BN is limited by its inherent brittleness. To overcome this problem, BN can be prepared into fibers. Within this goal, many researchers have focused on various methods to produce BN fibers [12–15]. However, all of these methods mentioned above require complicated and expensive apparatus or severe preparation conditions, resulting in the small amount production. Herein, our group has recently made very important progresses in the preparation of BN fibers using boric acid as boron source and melamine as nitrogen source, which results in facile and efficient synthesis of h-BN fibers. One of the main advantages of this approach is the

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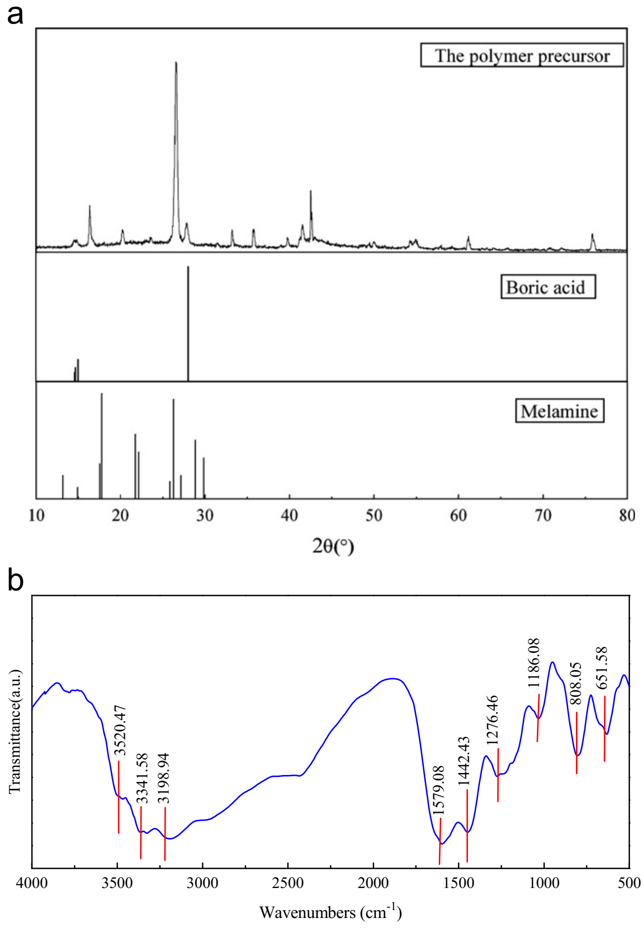

Fig. 1. XRD pattern (a) and FT-IR spectra (b) of the polymer precursor.

possibility of using melamine, a very cheap material as nitrogen source to prepare BN fibers.

2. Experimental

2.1. Raw materials

Boric acid (H_3BO_3, ≥99.8 mass%) and melamine ($C_3H_6N_6$, ≥99 mass%) were used as raw materials to prepare the polymer precursor. Nitrogen with high purity (≥99.999 mass%) was used for the reaction atmosphere to get BN fibers from the polymer precursor at high temperature.

2.2. Preparation of the precursor

The polymer precursor was prepared using H_3BO_3 and $C_3H_6N_6$ as raw materials at the ratio in accordance with the following equation:

$$6H_3BO_3+2C_3N_6H_6+3N_2 = 6BN+6H_2O+6CO+6NH_3+6NO \quad (1)$$

The two powders were mixed in a beaker. 400 ml deionized water was added in the beaker sealed by the plastic wrap and heated in a water bath. When the temperature reached 60 °C, 6.2 g H_3BO_3 was put into the beaker. 4.2 g $C_3H_6N_6$ was added into the beaker when the temperature reached 90 °C. The obtained solution was stirred by magnetic stirring to ensure that the two powders mixed uniformly and reacted completely. After that, the beaker was cooled to room temperature naturally and held for 12 h. Then the solution was filtered by pumping and dried to obtain white fibers as the polymer precursor.

2.3. Synthesis of h-BN fibers

The obtained polymer precursor was sintered in a vertical furnace at 1600 °C for 3 h in flowing nitrogen atmosphere with the flow rate of 2 l/min. When the furnace was cooled naturally to 300 °C, nitrogen was stopped and white fibers were obtained.

2.4. Phase and microstructure characterization

The phases were identified by X-ray diffraction (XRD; M21XVHF22, MAC Science, Yokohama, Japan) using Cu Kα radiation (40 KV, 20 mA, $\lambda=1.5406$ Å) in the angle range 10–80° with the scan speed of 2°/min. The morphology of the fibers was examined by thermal field emission scanning electron microscopy (FE-SEM; ZEISS SUPRATM 55, Germany). Fourier transformation infrared spectra in transmission mode were recorded on a Nicolet-Nexus 670 infrared spectrophotometer (FTIR; Nicolet-Nexus 670, Germany) with a spectral scanning range 4000–500 cm^{-1} using KBr wafer to analyze the structure of the polymer precursor and BN fiber. The thermoanalyser (TG/DTA, Nerzsch STA 449C, Germany) was heated to 1600 °C in nitrogen at a heating rate of 10 °C/min to investigate the reaction process. The sensitivity of the TG microbalance is ±0.1 μg, which makes it possible to record accurate weight changes during the reaction.

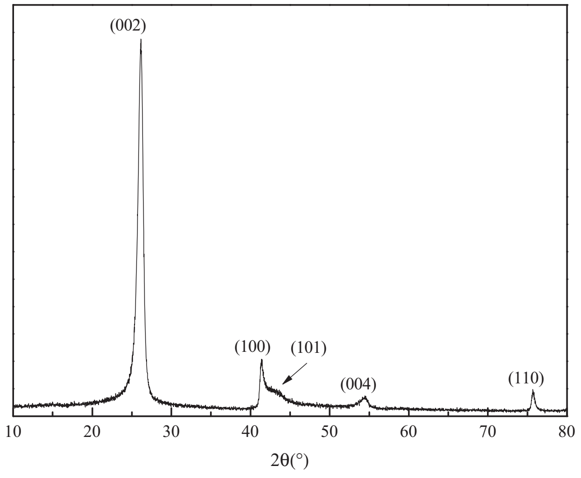

Fig. 2. XRD pattern of the synthesized BN fibers.

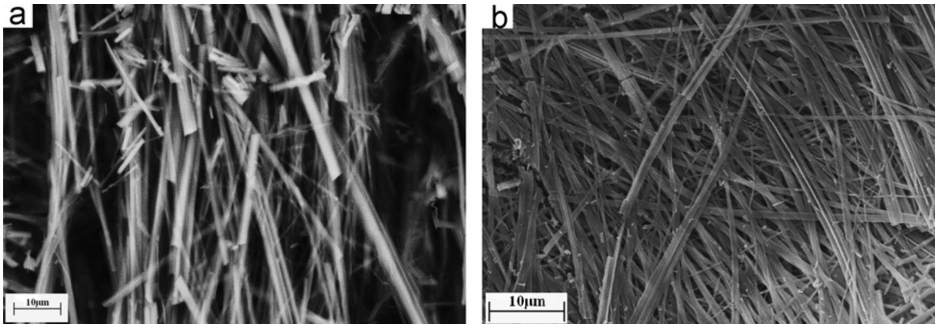

Fig. 3. SEM photos of the polymer precursor (a) and the BN fibers (b).

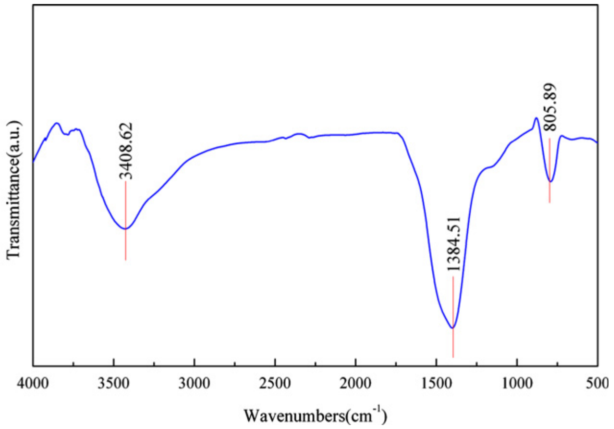

Fig. 4. FT-IR spectra of the BN fibers.

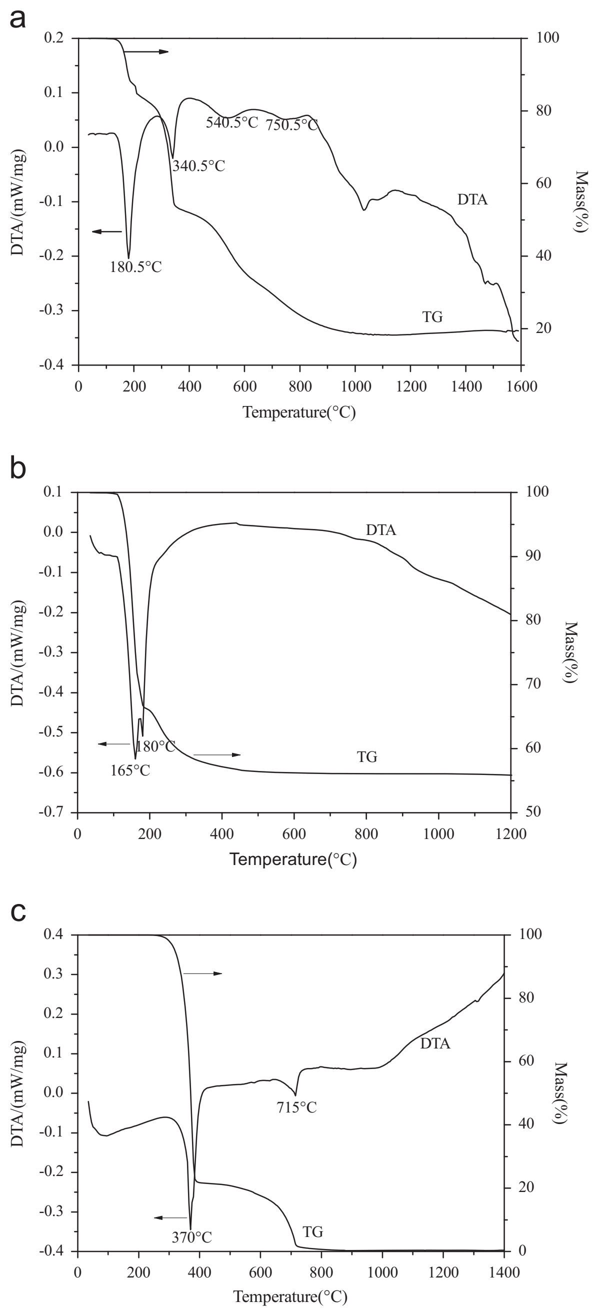

Fig. 5. TG-DTA of the precursor (a), H_3BO_3 (b) and $C_3H_6N_6$ (c) in flowing nitrogen at the heating rate of 10 °C/min.

3. Results and discussion

3.1. Phase and microstructure characterization

Fig. 1a shows the XRD patterns of the polymer precursor. Compared with the characteristic peaks of H_3BO_3 and $C_3H_6N_6$, it can be found that the phases of the precursor are not a simple mixture of the two powders. The FT-IR spectra of the precursor are shown in Fig. 1b. It can be seen that the precursor is composed of N–H (3341.58 cm^{-1}), O–H (3198.94 cm^{-1}), C–H (1442.43 cm^{-1}) and triazine ring (808.05 cm^{-1}). It may be a kind of crystalline polymer compound containing C, H, O and N elements. When the polymer precursor was heated at high temperature, the elements C, H and O left the precursor, forming a volatile product, leaving the elements B and N to form BN with high purity. The XRD pattern of BN fiber is shown in Fig. 2. All of the five peaks with *d*-spacings of 3.4102, 2.1762, 2.0747, 1.6844, and 1.2556 Å can be indexed as hexagonal BN ((002), (100), (101), (004), and (110) respectively) (JCPDS card no. 34-0421) [5,16]. No impurities such as B_2O_3 can be detected in the XRD patterns.

SEM images of the polymer precursor and the obtained BN fiber are shown in Fig. 3(a) and (b) respectively. As shown in Fig. 3(a), it can be clearly seen that the morphology of the polymer precursor was fiber-like with diameters of 2–5 μm and lengths of 20–500 μm. The morphology of the obtained

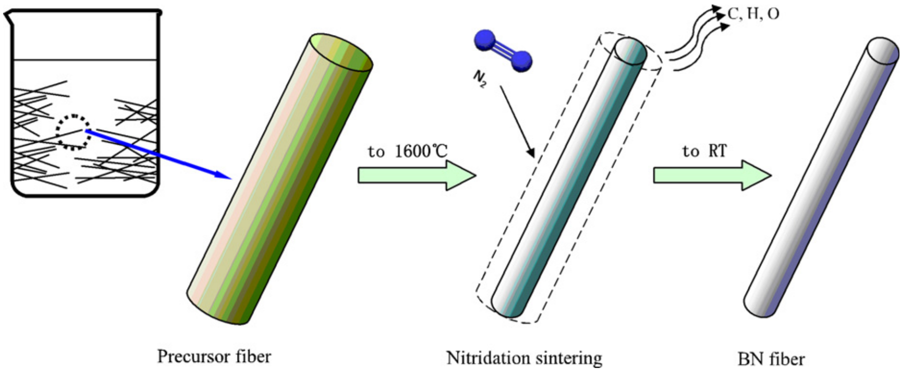

Fig. 6. Schematic diagram of the formation process of BN fibers with uniform morphology.

BN fiber shown in Fig. 3(b) is similar to that of the polymer precursor, illustrating that the BN fiber is obtained in situ from the polymer precursor. By comparison, the morphology of the obtained BN fibers exhibited much more uniformity but with smaller size. The size observed from the SEM image was 1–2 μm diameter and 200–500 μm length.

Fig. 4 shows the FT-IR spectra of the BN fiber. Two strong characteristic peaks are located at 805.89 and 1384.51 cm^{-1}. The absorption band at 1384.51 cm^{-1} is identified with the B–N stretching vibrations, and the absorption band at 805.89 cm^{-1} can be attributed to the B–N–B bending vibrations [13,14,17,18]. The broad absorption peak at 3408.62 cm^{-1} is due to absorbed water on the sample.

3.2. *Reaction mechanism*

Fig. 5a shows the thermal analysis of the polymer precursor from room temperature to 1600 °C in flowing nitrogen atmosphere. As shown in the DTA curve, two strong endothermic peaks were detected at 180.5 °C and 340.5 °C and two weak endothermic peaks were discovered at 540.5 °C and 750.5 °C. Combined with the TG–DTA curves of H_3BO_3 and $C_3H_6N_6$ in nitrogen atmosphere (Fig. 5b and c), the endothermic peak at 180.5 °C was caused by loss of the chemically adsorbed water of the precursor and part conversion reaction of H_3BO_3 to HBO_2. At 340.5 °C, HBO_2 completely lost all the structure water to produce B_2O_3. In addition, $C_3H_6N_6$ was decomposed partly. At higher temperature, the reaction to produce BN occurred with the loss of the element C, H and O, which caused the weight loss at higher temperature as shown in the TG curve (Fig. 5a). From 1000 °C, there was no mass change in the TG curve, indicating that the BN fibers may be produced from this temperature.

The maximum percentage of BN fibers can be calculated by Eq. (1) and the value was found to be 24.0%. As shown in Fig. 5, the experimental percentage of BN fibers was about 19.5%. Thus the productivity of BN fiber using this method was 81.3%, which is higher compared with the reported results using preceramic polymer method [18].

According to the above experimental results, the following reaction mechanism was proposed to explain the formation process of BN fibers using the precursor method. As shown in Fig. 6, H_3BO_3 reacted with $C_3H_6N_6$ to form the polymer precursor with the uniform morphology of fiber. The elements C, H and O were produced into gaseous compounds such as CO, NH_3, etc. at elevated temperature. These gaseous products were carried away by the flowing nitrogen atmosphere, leaving the elements of B and N to react, forming BN in situ with smaller size.

4. Conclusions

BN fiber was successfully fabricated by the polymeric precursor method using H_3BO_3 and $C_3H_6N_6$ as raw materials. This method is a simple process with low cost and high productivity. Therefore it is a promising method in practice. The morphology of the polymer precursor was fiber-like with diameters of 2–5 μm and lengths of 20–500 μm. The obtained BN fibers were produced from the polymer precursor in situ with 1–2 μm diameter and 200–500 μm length.

Acknowledgments

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References

[1] J. Economy, R.V. Anderson, Boron nitride fibers, Journal of Polymer Science Part C 19 (1967) 283–297.
[2] R.T. Paine, C.K. Narula, Synthetic routes to boron nitride, Chemical Reviews 90 (1990) 73–91.
[3] K. Watanabe, T. Taniguchi, H. Kanda, Direct-band gap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal, Nature Materials 3 (2004) 404–409.
[4] J.A. Perdigon-Melon, A. Auroux, C. Guimon, B. Bonnetot, B.N. Micrometric, Powders used as catalyst support: influence of the precursor on the properties of the BN ceramic, Journal of Solid State Chemistry 177 (2004) 609–615.
[5] L.X. Lin, Y. Zheng, Y. Zheng, K.M. Wei, Facile synthesis of hexagonal boron nitride fibers and flowers, Materials Letters 61 (2007) 1735–1737.
[6] J.B. Condon, C.E. Holcombe, D.H. Johnson, L.M. Steckel, The kinetics of the boron plus nitrogen reaction, Inorganic Chemistry 15 (1976) 2173–2179.

[7] T.S. Bartnitskaya, M.V. Viasova, T. Ya., N.V. Kosoiapova, Kostyuk, Formation of boron nitride during carbothermal reduction, Soviet Powder Metallurgy and Metal Ceramics 29 (1990) 990–994.

[8] C.K. Narula, R. Schaeffer, R.T. Paine, A. Datye, W.F. Hammetter, Synthesis of boron nitride ceramics from poly(borazinylamine) precursors, Journal of the American Chemical Society 109 (1987) 5556–5557.

[9] Y. Kimura, Y. Kubo, N. Hayashi, High-performance boron–nitride fibers from poly(borazine) preceramics, Composites Science and Technology 51 (1994) 173–179.

[10] L. Rao, R.B. Kaner., Rapid solid-state-precursor synthesis of crystalline boron nitride, Inorganic Chemistry 33 (1994) 3210–3211.

[11] V.L. Solozhenko, V.Z. Turkevich, G. Will, Synthesis of boron nitride by self-propagating reactions at high pressure, Journal of the American Ceramic Society 79 (1996) 2798–2800.

[12] L. Shi, Y.L. Gu, L.Y. Chen, Y.T. Qian, Z.H. Yang, J.H. Ma, Synthesis and morphology control of nanocrystalline boron nitride, Journal of Solid State Chemistry 177 (2004) 721–724.

[13] L.Y. Chen, Y.L. Gu, L. Shi, Z.H. Yang, J.H. Ma, Y.T. Qian, A room-temperature approach to boron nitride hollow spheres, Solid State Communications 130 (2004) 537–540.

[14] J.Q. Hu, Q.Y. Lu, K.B. Tang, S.H. Yu, Y.T. Qian, G.E. Zhou, X.M. Liu, J.X. Wu, Synthesis and characterization of nanocrystalline boron nitride, Journal of Solid State Chemistry 148 (1999) 325–328.

[15] L. Chen, M. Huang, T. Luo, et al., A low-temperature route to nanocrystalline boron nitride whiskers and flakes, Letters 58 (2004) 3634–3636.

[16] Y. Chen, J. Fitz Gerald, J.S. Williams, S. Bulcock, Synthesis of boron nitride nanotubes at low temperatures using reactive ball milling, Chemical Physics Letters 299 (1999) 260–264.

[17] C. Sun, C.L. Guo, X.J. Ma, L.Q. Xu, Y.T. Qian, A facile route to prepare boron nitride hollow particles at 450 °C, Journal of Crystal Growth 311 (2009) 3682–3686.

[18] T. Zhang, G. Wen, L. Xia, X.X. Huang, B. Zhong, X.D. Zhang, Synthesis of BN microspheres with high-purity via a polymer-chemical route, Scripta Materialia 63 (2010) 415–417.