Synthesis and formation mechanism of BN nanotubes catalyzed by Mg through ball milling and annealing process

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Abstract. In order to improve the yield of BN nanotubes prepared by ball milling annealing method, a small amount of magnesium was used as catalyst to synthesized boron nitride nanotubes. The results showed that boron nitride nanotubes with high yield, high purity and uniform size were synthesized. The morphology of the synthesized BNNTs is bamboo-like and cylinder-shaped. The diameter of them is about 50 to 150 nm and most of them are 100nm. The length of them is dozens of microns. The existence of end particles indicates that the growth mechanism of BNNTs can be attributed to a gas-liquid-solid growth model. The magnesium catalyzed preparation of boron nitride nanotubes has stable process, high yield and high purity, which is expected to be a good method for large-scale preparation of boron nitride nanotubes.

Keywords: Boron nitride nanotubes; Ball milling and annealing; Magnesium catalysis; Mechanism.

1 Introduction

Since the theoretically predicted in 1994[1], boron nitride nanotube(abbreviated as BNNTs) has received considerable attention for its remarkable properties such as good chemical inertness, stable insulation characteristic, high thermal conductivity and outstanding mechanical strength [2-3]. Various methods such as chemical vapor deposition (CVD) [4], arc-discharge [5-6], laser ablation [7], plasma-jet [8-9] and substitution of carbon nanotubes(abbreviated as CNTs) [10-11] have been developed to synthesize BNNTs. However, all these methods can't meet the need of high yields. Ball milling and annealing method, which was first proposed by Chen [12], is a widely used approach for producing boron nitride nanotube [13-15]. The main merits of this method are available in low reaction temperature and high yield. Bamboo like and cylindrical BN nanotube have been synthesized by our group through this method [16]. However, the size of the prepared nanotube is not uniform and the yield of them was relatively low because there was no special catalyst was added.

In order to further improve the yield of the BN nanotube, different catalyst such as Fe, Mg, Co, Ni, Fe_2O_3 and C10H10Fe were used. The results indicate that the highest yield was obtained when Mg was used as catalyst. Although some literature [17] have reported

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similar methods to prepare BN nanotube, there are still some problems such as high dosage of catalyst, higher reaction temperature and longer reaction time, which increase the cost to a certain extent. In this paper, the further optimization preparation process of BNNTs synthesized by ball milling and annealing method using magnesium(abbreviated as Mg) as catalyst will be reported. The effect of dislocation density on the formation of BN nanotube with different morphology was discussed. The chemical reaction process and growth mechanism were analyzed also.

2 Experiments

B_2O_3 powder with a purity of 99.99% and Mg powder with a purity of 99.99% were first milled together in a planetary ball mill. The material of ball mill tank and ball is stainless steel. The diameter of the stainless ball is 10mm, 8mm and 5mm. The ball milling process was carried out under the protection of high purity nitrogenin. The ball mill speed is 280 rpm and the ball mill time is 4h. The weight ratio of the milling balls to B_2O_3 powder was 100:1. The molar ratio of boron oxide and Mg powder is 30:1. The milled B_2O_3 powder doped with Mg powder was then annealed in a GLS1600X tube furnace at 1300℃ for 2h under a high purity ammonia gas flow. The ammonia gas flow was controlled at 50ml/min.

Digital photo of the product was taken by Huawei mobile phone. Crystalline structure of the product was researched by means of X-ray diffraction analysis (XRD) using Cu Ka radiation (λ=0.15418 nm) at room temperature. Morphology of the product was observed by S-4800 scanning electron microscope (SEM) and JEM-200CX transmission electron microscope (TEM). The X-Ray energy dispersive spectroscopy (EDS) attached to S-4800 scanning electron microscope was employed to determine chemical composition of the sample. The selected area electron diffraction (SAED) of the sample was performed on the TEM. JEM-2100F high-resolution transmission electron microscope (HRTEM) operated at 200 KV was employed to observe the sample carefully. The element distribution was detected by energy dispersive spectrometer attached to high resolution electron microscope.

3 Results and discussions

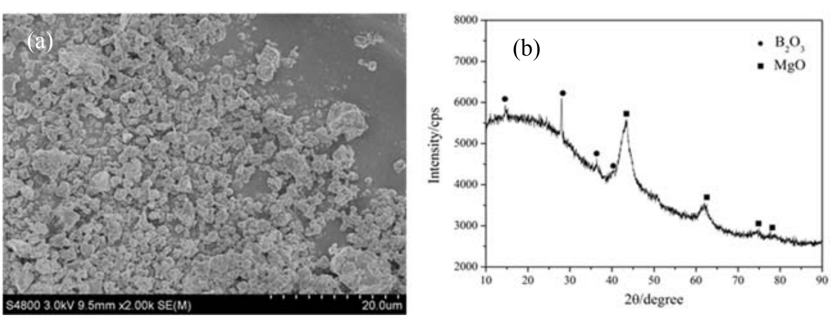


Fig. 1. SEM image (a) and XRD patterns (b) of B_2O_3 milled for 4h.

Fig.1 (a) and (b) were SEM image and XRD pattern of B_2O_3 powder milled in high pure N_2 for 4h respectively. Fig.1 (a) shows that the particle size is about 2~10 μm after mixed ball milling of boron oxide and magnesium powder. The surface of the particles is not smooth due to the activation of ball milling. Some weak peaks of B_2O_3 still existed in Fig.1 (b) indicated that most B_2O_3 powder was changed into amorphous and little of them was still crystal after milled for 4h. Obvious magnesium oxide (MgO) peaks showed that Mg powder changed into MgO after ball milling.

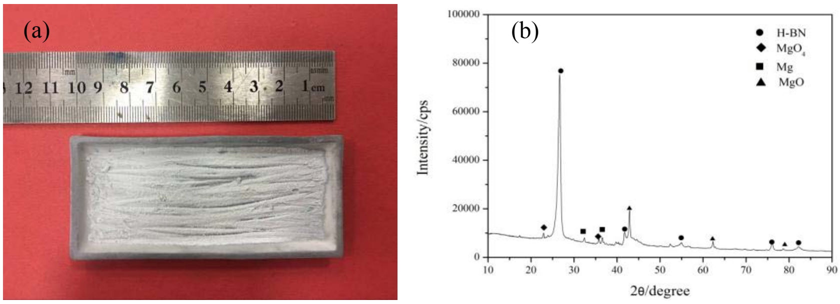
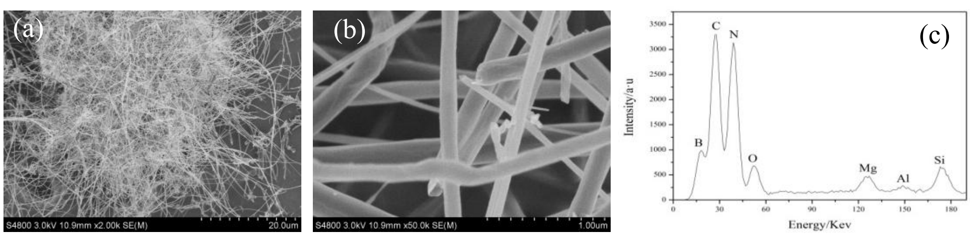


Fig. 2. Digital photo (a) and XRD pattern (b) of the product.

Fig.2 (a) was the digital photo of the sample after annealing at 1300℃ for 2 hours. Loose white powder can be observed covering the whole porcelain boat, which indicated that the nitriding reaction of the B_2O_3 precursor was very thorough. All the precursor was converted into BN nanotube in the presence of Mg. Calculation indicated that the yield of the BNNTs is up to 85% and the purity of them is over 90%. Fig.2 (b) was the XRD pattern of the products. The analysis shows that the product is mainly composed of H-BN and a small amount of impurities such as MgO_4, Mg, MgO. The diffraction peak of H-BN is sharp and clear, which indicates that the crystallinity of the product is good. The diffraction peak of a small amount of Mg and MgO is caused by the addition of catalyst magnesium.



(a)Low magnification image, showing homogeneous one-dimensional fibrous structure in large quantities. (b) High magnification image, showing smooth surface and uniform diameter. (c) EDS spectrum of the product

Fig. 3. SEM images and EDS spectrum of the product.

Fig.3 shows the SEM images and EDS spectrum of the product after annealing. It can be seen from Fig.3 (a) that the product consists of a large quantity of homogeneous one-dimensional fibrous substances with a length of about tens of microns. Fig.3 (b) was the enlarged SEM image of the product, which shows that the surface of the fibrous substances is smooth. The diameter of them is range from 50nm to 150nm and most of them are about 100nm. Fig.3(c) was the EDS spectrum of the product. The result showed that the product was mainly composed of B and N elements, and the atomic ratio is 37.5:41.55, approximately 1:1, which is close to the chemical equivalence ratio of BN, indicating that the product is composed of BN. The stronger C peak comes from the conductive adhesive used for sample preparation. Oxygen is a common impurity in the preparation of BN nanomaterial, which may be slightly oxidized or adsorbed by the products exposed to air. In addition, there are Mg, Al and Si elements. Among them, Mg is from the catalyst added, while Al and Si may be impurities introduced by ceramic boat.

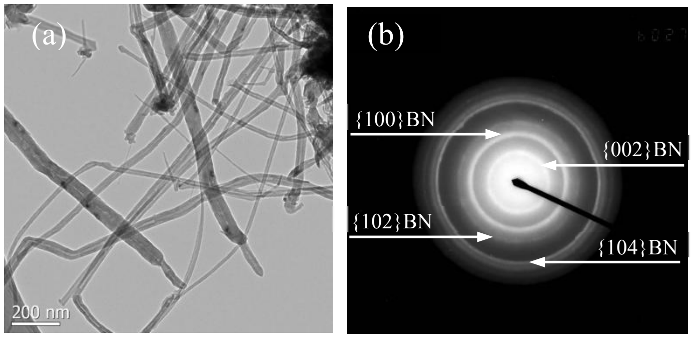


Fig. 4. TEM images(a) and SAED pattern(b) of the product.

Fig.4 was the TEM image and corresponding SAED pattern of the product. It can be found from Fig.4 (a) that many hollow tubular structures with different diameter can be observed, indicating that the product was BN nanotubes. The morphology of the BN nanotube can be divided into two kinds, bamboo-like and cylinder-shaped. Obvious periodic bamboo knot can be found in bamboo-like BN nanotube with large diameter, but it is difficult to found a bamboo knot in cylinder-shaped BN nanotube with small diameter. The larger the tube diameter is, the shorter the bamboo spacing is. The smaller the pipe diameter is, the longer the bamboo spacing is. This phenomenon makes the nanotubes with small diameter look like cylinders [16].

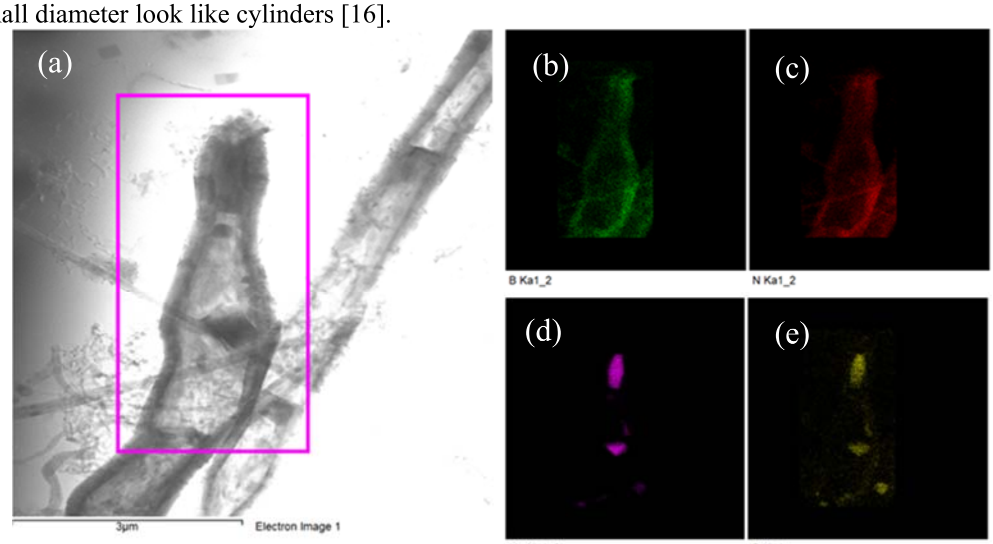


Fig. 5. TEM image (a) and corresponding element mapping of boron(b), nitride(c) , magnesium(d) , oxygen(e).

In order to investigate the formation mechanism of the synthesized BN nanotubes, keeping other parameter unchanged, the B_2O_3 precursor doped with Mg powder annealed for 0.5h under high purity ammonia gas were observed by JEM-2100F microscope. TEM image and elemental scanning distribution (Energy filtered imaging) in selected areas of the sample was shown in Fig.5 (a) to Fig. 5 (e). Fig. 5 (a) indicated that the product is bamboo like tubular structure wrapped with particles. Fig. 5 (b) to Fig. 5 (e) was the surface scanning distribution of B, N, Mg, O, respectively. It can be found that B, N element occurs on the tube wall while Mg, O element occurs in the tube. So it can be concluded that the product is boron nitride nanotubes, in which the encapsulated particles are magnesium oxide.

From the XRD spectra of the precursor and the above analysis results, it can be seen that the precursor powder is composed of ball milling activated boron oxide powder and magnesium oxide powder formed by the oxidation of magnesium powder during ball milling. It is inferred that the possible chemical reactions during annealing process are as follows:

$$NH_3(g) \rightarrow N_2(g)+H_2(g) \quad (1)$$

$$B_2O_3(g)+3H_2(g) \rightarrow 2B(s)+3H_2O(g) \quad (2)$$

$$B(s)+MgO(s) \rightarrow B_2O_2(g)+Mg(l) \quad (3)$$

$$B_2O_3(l)+3Mg(l) \rightarrow 2B(s)+3MgO(s) \quad (4)$$

$$B_2O_2(g)+2NH_3(g) \rightarrow 2BN(s)+2H_2O(g)+H_2(g) \quad (5)$$

$$Mg(s)+H_2O(g) \rightarrow MgO(s)+H_2(g) \quad (6)$$

NH_3 will be decomposed into H_2 and N_2 when it is in a high temperature environment (as shown in reaction equation 1). H_2 will react with B_2O_3 to form boron and water vapor (as shown in reaction equation 2). From the previous analysis, it can be seen that the Mg powder added during ball milling has been thoroughly oxidized to MgO, and the boron element produced during these process will further react with MgO to obtain the metastable phase B_2O_2 gas and the important reducing agent Mg (e.g. reaction equation 3). The molten Mg reduces boron oxide to boron and magnesium oxide (e.g. reaction equation 4) at high temperature. This process is reciprocating and will be accelerated gradually with the oxidation-reduction reaction, making a large number of B_2O_3 developed into boron in the positive direction of chemical equilibrium, and then into metastable B_2O_2 gas. Among them, Mg metal plays the role of reducing agent and accelerator. Its existence not only accelerates the overall chemical reaction speed, but also effectively promotes the chemical equilibrium to move towards the direction of the formation of B_2O_2. This is also the key reason for the more efficient and stable method of preparing BNNTs than Fe catalyst. No Mg but MgO particles were found in the tube and the end of the synthesized BNNTs (as shown in Figure 6). This phenomena indicated that part of the Mg metal also generates MgO and H2 (e.g. reaction equation 6) under the action of water vapor, so that all Mg particles in the final product are converted into MgO. In addition, the existence of end particles also indirectly proves that the growth mechanism of BNNTs is a gas-liquid- solid growth model.

4 Conclusions

BNNTs with high yield, high purity and uniform size were synthesized from boron oxide by ball milling and annealing process using Mg as catalyst. The morphology of the synthesized BNNTs is bamboo-like and cylindrical. The diameter of them is about 50 to 150nm and most of them are 100nm. The longest one is up to several micrometers. Calculation indicated that the yield of the BNNTs is up to 85% and the purity of them is over 90%. TEM image and elemental scanning distribution in selected areas of the sample show that the growth mechanism of BNNTs can be attributed to a gas-liquid-solid growth model. For the stable process, high efficiency, high yield and high purity, Mg catalyzed preparation of BNNTs is expected to be a good method for large-scale preparation of boron nitride nanotubes.

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