Research Article

Synthesis of *h*-BN by the Combustion of B/KNO₃/Octogen Mixture under Nitrogen Atmosphere

Song-qi Hu, Yin Wang, and Lin-lin Liu

Science and Technology on Combustion, Internal Flow and Thermal-Structure Laboratory,
Northwestern Polytechnical University, Xi'an 710072, China

Correspondence should be addressed to Lin-lin Liu; lll@nwpu.edu.cn

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Hexagonal boron nitride (*h*-BN) powders were fabricated by the combustion synthesis with B/KNO₃/HMX (octogen) mixtures as reactants. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were adopted to investigate the phase composition and the chemical composition of the products, respectively. The morphology and resistance to oxidation were studied by scanning electron microscopy (SEM) and thermogravimetry (TGA), respectively. The characterization results showed that the *h*-BN which was produced through this method has high purity and exhibits excellent resistance to oxidation. The purity of *h*-BN is improved with the increasing content of HMX in reactants with boron carbide (B₄C) and boron oxide (B₂O₃) as main impurity, but conversely, the yields are obviously decreased. Taking the comprehensive consideration of the purity and the yields together, the optimal molar ratio of B/KNO₃/HMX is 10 : 1 : 4. In addition, the experimental results indicated that the crystalline grain size grows with the increasing content of HMX. The method explored in this study does not need expensive processing facilities and equipment, which is a preferable approach for the laboratory to prepare *h*-BN of high purity.

1. Introduction

Hexagonal boron nitride (*h*-BN) is the most stable crystalline form of boron nitride with excellent thermal and chemical stability. The crystal structure of *h*-BN is similar with the structure of graphite which provides excellent lubricating properties. Therefore, the powder of *h*-BN is usually employed as a kind of lubricant [1]. *h*-BN ceramic has many unique properties so that it could be used as ceramic for parts of high-temperature equipment [2]. The dense shapes of *h*-BN formed by hot press and with boric oxide as additives can be easily machined in the desired shapes because of the platy hexagonal crystals and their orientation during the hot press consolidation [3]. Furthermore, *h*-BN is also widely used to improve the machinability of AlN, SiC, Si₃N₄, Al₂O₃, etc. [4–7]. Therefore, *h*-BN is an important additive of ceramics.

In industry, *h*-BN powder is usually obtained by the reaction of boron oxide (B₂O₃) or boric acid (B(OH)₃) with ammonia (NH₃) or urea (CO(NH₂)₂) under nitrogen

atmosphere in the presence of activated carbon or carbon [8, 9]. The concentration of *h*-BN can achieve up to 98% after removing the excess boron oxide in the products through this method. *h*-BN could be applied as the coating material because of the excellent thermal and chemical stability, and the deposited thin film of *h*-BN is usually obtained through the chemical vapor deposition (CVD) [10].

Self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) is an effective way for preparing the ceramic materials [11]. SHS is also an economical and preferable approach for the preparation of ceramic as it avoids the need for expensive processing facilities and equipment. There have been many research studies concerning the fabrication of *h*-BN and ceramic composite containing *h*-BN by combustion synthesis in recent years [12–14].

The present work attempted to prepare *h*-BN by combustion synthesis. Concerning that the chemical property of boron oxide is quite stable and the unreacted boron oxide is very difficult to be removed, boron is selected as one of the

raw materials. The nitriding of boron needs nitrogen and heat; therefore, some explosives can be used as the ideal reactant. There is less oxygen and more nitrogen in cyclo-tetramethylene tetranitramine (HMX), and the combustion of HMX releases a lot of heat, so more *h*-BN is expected to be produced while less boron to be oxidized when HMX is employed as a raw material. Considering the vigorous combustion reaction between boron and potassium nitrate (KNO_3), high combustion heat is generated ($\sim 7,000 \text{ kJ}\cdot\text{g}^{-1}$), so adding proper amount of KNO_3 promotes the subsequent reaction [15]. In addition, appropriate amount of KNO_3 can increase the yields of resultant as reactants [16].

2. Method and Materials

2.1. Raw Materials. The amorphous boron powder from Dandong Chemical Engineering Institute Co., Ltd., (>95% in purity, $1 \mu\text{m}$) was used without any further purification. KNO_3 of analytical grade was purchased from Xuzhou Jingke Reagent Instrument Co., Ltd. Cyclotetramethylene tetranitramine (HMX) of analytical grade was obtained from Gansu Baiyin silver chemical materials plant. The pure *h*-BN from Aladdin Industrial Corporation, Shanghai, China (>99.9% in purity), was used for comparison with a standard *h*-BN sample in the study.

2.2. Synthesis. Boron reacts with KNO_3 vigorously to generate potassium borate, and then the yield will be very low when the content of KNO_3 in the reactants is too high. Therefore, the optimal molar ratio of boron and KNO_3 in this study is set as 10 : 1. The nitrogen needed to form *h*-BN is mainly from HMX. One possible reaction mechanism is as follows:

In the chemical reactions, the nitrogen atoms in HMX are eventually converted to boron nitride. Theoretically, the maximum yields are achieved when the molar ratio of B/HMX is about 8 : 1 by the nitrogen conservation. In addition, boron powder is difficult to dissolve in water, and the boron powder which is not fully reacted cannot be removed in the process purification of boron nitride. In order to ensure the high purity of boron nitride, the reactant HMX overdose is required. Thus, the molar ratio of B/ KNO_3 /HMX is set as 10 : 1 : 3, 10 : 1 : 3.5, 10 : 1 : 4, and 10 : 1 : 4.5, respectively. The reactant powders were obtained by the mixing of B/ KNO_3 mixture and HMX in a planetary ball mill (Focucy, F-P400) for an hour.

The reactant powders were pressed under 10 MPa for about 30 min, and the test specimens were prepared in a cylindrical shape with diameter of 8 mm and height of 20 mm. Combustion synthesis was conducted in a combustion chamber under high purity (99.99%) nitrogen of 2 MPa. The products were washed with water, and then the

subsequence filtration was done after the cooling in the combustor. The insoluble products after drying were obtained as the samples to be characterized.

2.3. Characterization. The morphology of the products was observed by scanning electron microscopy (SEM, FEI Quanta 600F, USA). The phase composition was identified by X-ray diffraction (XRD, Bruker, D8 Advance, Germany); the scattering angles (two theta) is $5\text{--}60^\circ$ with $\text{Cu } \alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The chemical composition was determined by X-ray photoelectron spectroscopy (XPS, Thermo fisher, K-Alpha, USA). The resistance to oxidation of the products was tested in thermogravimetry (Mettler Toledo, TGA/DSC 1, Switzerland), each sample weighing 3 mg was placed in alumina crucible and heated from 50°C to 1500°C at a $10^\circ\text{C}\cdot\text{min}^{-1}$ heating rate under air atmosphere.

3. Results and Discussions

3.1. X-Ray Photoelectron Spectroscopy. The surface chemical state of the samples was valuated with XPS, and the atomic composition of B, N, C, and O in the samples is shown in Table 1.

Table 1 suggests that the B : N atomic ratio in C1 sample and C2 sample is 1.49 : 1 and 1.43, and there are also a lot of C atoms in the two samples, so there may be some boron carbide and carbon impurity in the two samples. The B : N atomic ratio is near 1 : 1 for C3 sample and C4 sample, which indicates that C3 and C4 have high purity of *h*-BN.

The XPS experiments show the similar spectrum for C1 sample and C2 sample and also for C3 sample and C4 sample, and only the B1s, N1s, C1s, and O 1s binding energies of sample C1 and C3 are shown in this paper.

Figure 1 shows that the B1s peak could be split into a doublet, and the peaks centered at approximately 190.6 eV and 192.5 eV, which are corresponding to boron nitride and boron oxide, respectively [17, 18]. The C1s spectrum is split into three peaks, the binding energy at 283 eV is assigned to B_4C , and the other two high binding energy shoulders are related to the surface contamination [19]. In addition, the N1s peak at 398 eV is also ascribed to *h*-BN, and the O1s peak also results from the measurement of XPS. Therefore, *h*-BN is the major material in C1 sample and C2 sample, and the principal impurities are B_4C and B_2O_3 .

Figure 2 shows that the B1s peak and N1s peak of C3 sample are symmetrical and could not be split into a doublet, and the binding energy at 190.6 eV and 398 eV is assigned to *h*-BN. In addition, C1s peak and O1s peak are originated in the surface contamination due to exposure to ambient conditions, which is similar to the results of C1s peak and O1s peak in Figure 1.

The XPS results of C1 and C3 samples also suggest that the purity of *h*-BN can be improved by increasing the content of HMX in the reactants. Boron reacted with potassium nitrate vigorously during the combustion process with the main products of potassium borate. Nitrogen oxides (mainly NO_2 and NO) were produced during the combustion of HMX, and these nitrogen oxides could react with

TABLE 1: Atomic composition of B, N, C, and O.

Sample	Molar ratio of B/KNO ₃ /HMX	B/%	N/%	C/%	O/%
C1	10:1:3	40.24	26.94	29.96	2.86
C2	10:1:3.5	43.07	30.15	21.22	5.56
C3	10:1:4	43.63	41.16	10.62	4.59
C4	10:1:4.5	43.96	44.84	8.22	2.98

FIGURE 1: XPS results of C1 sample.

boron to generate *h*-BN. As there is oxygen in HMX, more boron oxide and boron acid will be produced if there is more HMX in the reactant which will result in the lower yields.

3.2. SEM. SEM images of the samples are shown in Figure 3.

Figure 3 indicates that all the products fabricated by combustion synthesis are thin flakes. C1 sample and C2 sample are composed of agglomerated particles with irregular small particle size, but C3 sample and C4 sample are both composed of single particle. In addition, the particle size of *h*-BN crystalline grain for C1 sample and C2 sample is sub-micron while C3 sample and C4 sample have only a few microparticles. Due to the large number of irregular particles

on the surface of C1 and C2 samples, the specific surface area of C1 and C2 samples is larger than that of C3 and C4 samples, which may lead to the lower antioxidant capacity of C1 and C2 samples than that of C3 and C4 samples. From the particle shape, these irregular particles in C1 and C2 samples may not be the same substance as the single particles in C3 and C4 samples. With the increase of HMX content, the particle shapes in the sample tend to be consistent. Therefore, it could be concluded that both the purity and the size of crystalline grain increase with the increase of the content of HMX.

3.3. X-Ray Diffraction. After filtration and drying, samples of C1 and C2 are solid powder with light grey in color while

FIGURE 2: XPS results of C3 sample.

white in color for C3 and C4 sample. Figures 4 and 5 show the XRD patterns of the solid products.

Figures 4 and 5 show that the main phases in the C1 sample and C2 sample are *h*-BN (hexagonal, PDF-34-0421) and B₄C (rhombohedral, PDF-35-0798), and only *h*-BN for C3 sample and C4 sample are consistent with the results of XPS. Therefore, *h*-BN can be prepared by this method.

Similarly, *h*-BN and B₄C are materials with high chemical and thermal stability. It is difficult to separate B₄C from *h*-BN. Based on the results of XRD and XPS, in this case, it is evident that B₄C exists as impurity when the content of HMX is low. Considering the difficulties of removing B₄C, the experiment results show that it is impossible to enhance the purity by the removal of B₄C, and what can be applied is only decreasing the generation of B₄C through the increase of HMX. However, the yields are calculated from the obtained products and the theoretical ones, and it can be decreased obviously with the increase of HMX. Considering both the purity and the yields, the optimal molar ratio of B/KNO₃/HMX is chosen as 10:1:4 in this study.

The method represented in this paper does not need expensive processing facilities and equipment, and the *h*-BN with high purity could be easily obtained only after the simple processing of the combustion products. In addition, the only solution used in this method is water, and the pollution of organic solvent could be avoided efficiently.

Therefore, it is a preferable approach for the laboratory to prepare *h*-BN of high purity.

3.4. Thermogravimetry. The TGA results of C1 sample and C3 sample under air atmosphere are shown in Figure 6.

Figure 6 indicates that C1 sample begins to gain mass at about 600°C, and the mass of sample increases obviously when the temperature reaches about 1200°C. The mass of C1 sample increases slowly within the temperature range from 1200 to 1400°C, but decreases rapidly when the temperature is higher than 1400°C. There is some B₄C in C1 sample which is much easier to be oxidized under higher temperature, so the mass gain is mainly due to the oxidation of B₄C (R4) below 1200°C and the oxidation of *h*-BN from 1200 to 1400°C (R5). The oxide on the surface of the block the oxidation process of the sample, and when the temperature higher than 1400°C, the mass of sample decreases rapidly due to the evaporation of boron oxide on the C1 sample surface.

Different from samples of C1, the TGA curves of C3 samples and pure *h*-BN almost coincide with each other, and they begin to gain mass at about 1000°C which shows the

FIGURE 3: Morphology of the samples.

FIGURE 4: XRD patterns of C1 and C2 samples.

FIGURE 5: XRD patterns of C3 and C4 samples.

same resistance to oxidation performance of C3 sample and the pure *h*-BN. This indicated that the purity of C3 sample was higher than that of C1 sample, which was also consistent with the XRD test results. Therefore, the resistance to oxidation

performance can meet the requirement of the preparation of high-temperature *h*-BN-based ceramics. In addition, the mass loss in TGA curves ascribed the evaporation of boron oxide produced by the oxidation of B_4C and *h*-BN.

FIGURE 6: TGA curves of C1 and C3 sample under air atmosphere.

4. Conclusions

h-BN with high purity could be prepared by combustion synthesis with B/KNO₃/HMX mixture as the reactant, and the *h*-BN prepared in this method exhibits excellent resistance to oxidation performance. The purity of *h*-BN is improved but the yields are decreased obviously with the increase of HMX in the reactants, and the optimal molar ratio of B/KNO₃/HMX is 10 : 1 : 4. As the method is easy and does not need expensive facilities, it is a preferable approach for the laboratory to prepare *h*-BN of high purity.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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