Combustion synthesis of boron nitride via magnesium reduction using additives

Shyan-Lung Chung[a,b,*], Yu-Hsiang Hsu[a]

[a]Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan, ROC
[b]Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan, 70101, Taiwan, ROC

Abstract

This study is aimed at enhancing the product yield in combustion synthesis of h-BN using Mg reduction of B_2O_3 as the boron source under a low N_2 pressure by using additives. The reactant powders and the additives were placed in perforated aluminum containers without pressing. Due to a loose and highly porous structure of the powder stack, the surrounding N_2 can penetrate easily into it and the N_2 generated by NaN_3 or $C_3H_6N_6$ escapes easily, addition of these two additives only increases slightly the product yield in the low content region but decreases the product yield in the high content region due to decreasing temperature. Addition of inert particles (i.e., MgO or BN) increases the product yield only when the temperature is higher than the melting point of boron, under which coalescence of molten boron is suppressed due to capillary spreading of the molten boron on the particles. When the temperature is lower than the melting point of boron, addition of the inert particles decreases the product yield because of their cooling effect. NH_4X (X=Cl or Br) was found the most effective in enhancing the product yield because it creates an easier route for the nitridation of boron by first converting boron to BX_x, which then reacts with N_2 under the reduction of H_2. A product yield of 67% was achieved by simultaneous addition of NH_4Cl and BN under a N_2 pressure of 1.6 MPa.
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1. Introduction

Hexagonal boron nitride, h-BN, has long been acknowledged as an important industrial material due to its unique combination of many interesting properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, chemical inertness and high resistance to thermal shock and corrosion [1–3].

Conventionally, h-BN has been widely used in fabrication of crucibles, refractories, lubricants, insulators and cosmetics [1–3]. Recently, h-BN has been discovered to have potential applications as a hydrogen storage medium [4–7], high temperature reaction catalyst support [8–10], filler in high thermal conductivity

composites [11,12], adsorbent in wastewater treatment [7], nanovector for targeted drug delivery [13] and deep ultraviolet light emitter in optoelectronics [14,15].

Many methods have been developed for synthesis of hexagonal BN including classical high-temperature routes [1,3] (e.g., reaction of boron oxide and ammonia [16], direct nitridation of boron with N_2 [1] and carbothermal reduction and nitridation of boron oxide [17]), vapor deposition methods (e.g., reaction of boron trichloride and ammonia [18]), condensed-phase pyrolysis techniques (e.g., thermal decomposition of borazene or bisborazinylamine [19]), solid-state metathesis [7,20,21], pyrolysis [4,10,12,22] and combustion synthesis [23–25]. Most of these methods have to be carried out under a high temperature heating or a high N_2 pressure and require a long processing time. Many of these methods also involve the use of oxygen or moisture sensitive reactants and some of the methods suffer from low production yield. These problems either pose difficulty in mass production or result in a

*Corresponding author at: Department of Chemical Engineering, National Cheng Kung University, Tainan, 70101, Taiwan, ROC. Tel.: +886 6 2757575 62654; fax: +886 6 234 4496.

E-mail address: slchung@mail.ncku.edu.tw (S.-L. Chung).

high production cost and thus hinder the practical application of the methods.

In our previous study [23], a combustion synthesis process was developed for synthesis of h-BN by using boron particles as the boron source. By adding additives (i.e., NaN_3 and NH_4Cl or NH_4F) into the reactants and wrapping the reactant compact with an igniting agent, a high product yield (up to 82%) was obtained under a low N_2 pressure (1.0 MPa). In spite of many advantages (e.g., simple processing, low energy consumption, low N_2 pressure, fast reaction and high product yield), this process suffers from using costly boron source and requiring wrapping of igniting agent. (The latter poses difficulty in mass production.) Borovinskaya et al. [24,26] developed a combustion synthesis method for synthesis of h-BN by using Mg reduction of B_2O_3 as the boron source. Although the cost of the boron source was greatly reduced, the product yield was low (< 30%) even though a high N_2 pressure (> 6 MPa) was applied.

This study was aimed at developing a combustion synthesis process for synthesis of h-BN under a low N_2 pressure by using Mg reduction of B_2O_3 as the boron source. The product yield was found to be significantly improved by adding proper amounts of certain additives. The effects of several different types of additives on the product yield were thus investigated to obtain the general characteristics of the additives capable of significantly enhancing the product yield. A combustion process and a reaction mechanism were also proposed based on the experimental results.

2. Experimental

Listed in Table 1 are the characteristics of the reagents used in the present study. B_2O_3 and Mg powders were used as the primary solid-state reactants (in which Mg reduction of B_2O_3 serves as the boron source). The additives under study can be

classified into four categories: (I) those generating N_2 after decomposition, i.e., NaN_3 and $C_3H_6N_6$; (II) inert particles, i.e., MgO and BN; (III) those generating hydrogen halides (HX, X=Cl or Br), i.e., NH_4Cl and NH_4Br; (IV) combinations of two additives, i.e., NH_4Cl and NaN_3 or BN. In all the experiments presented in this work, the amounts of B_2O_3 and Mg were kept at the stoichiometric ratio, i.e., B_2O_3:Mg=1:3. (All the reactant compositions were expressed as molar ratios.) B_2O_3, Mg and desired amounts of one or two additives were thoroughly mixed and then poured into a perforated aluminum container. (No pressing was applied to the powder and the bulk density of the powder stack was 0.65–0.77 g/cm³.) The perforated aluminum container was cylindrical in shape with 30 mm in diameter and 55 mm in length. It was made of perforated aluminum sheet with a thickness of ~15 μm, hole diameters of 1–3 mm and a hole area of 30–40% of the sheet area. The combustion synthesis reactor used in the present study has been described and shown schematically in our previous studies [27,28] and thus is not repeated here. The perforated aluminum container (containing the reactant powders) was placed on a height adjustable stage which was adapted so that the top surface of the powder stack was about 5 mm below the tungsten heating coil. The reactor was evacuated to 65 Pa by flushing with nitrogen between the evacuations. After the evacuation, the reactor was backfilled with nitrogen to the desired pressures. The combustion reaction was ignited by heating the top surface of the powder stack for ~10 s by applying an electrical power of ~1.5 KW to the heating coil.

Variation of temperature during combustion reaction was measured by using 0.25 mm diameter W-5%Re-W-26%Re thermocouples. The thermocouples, insulated with 1.2 mm diameter alumina tubes, were inserted into the powder stack at appropriate depths. As shown by the insert in Fig. 1, thermocouple A was inserted into the center of the powder stack to measure the temperature variation at the center and thermocouple B was inserted ~1 mm below the outer surface to measure the temperature variation in the outer region of the powder stack. After the combustion reaction, the perforated aluminum container, which became tiny particles (due to melting)
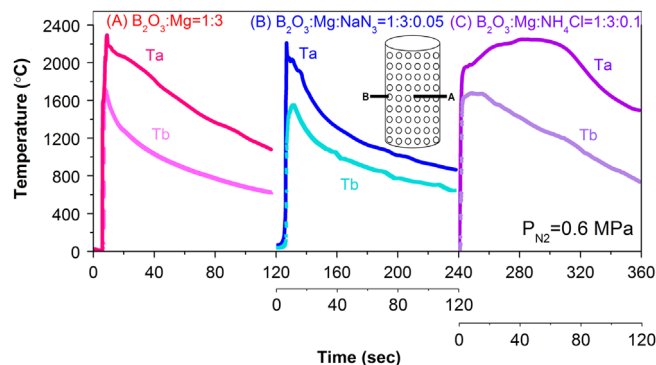
Table 1
Characteristics of the reagents used in the present study.

Category	Reagent	Particle size (μm)	Melting point (°C)	Purity (%)	Source
Reactant	B_2O_3	−60 mesh	450	> 97.5	Alfa Aesar, USA
	Mg	~20[a]	650	99	Nihon Shiyaku, Japan
	N_2	gas		99	Yun Shan, Taiwan
Additive	(I) generating N_2 after decomposition				
	NaN_3	~150[a]	275[b]	98	Showa, Japan
	$C_3H_6N_6$	…	345[b]	99.5	Showa, Japan
	(II) inert particles				
	MgO	−325 mesh	2800	99	Nihon Shiyaku, Japan
	BN	~8[a]	2600[b]	99	Fnami, Taiwan
	(III) generating hydrogen halides				
	NH_4Cl	…	338[b]	99.5	Panreac, Spain
	NH_4Br	…	452[b]	99	Fluka, Switzerland

[a] d_{50}.
[b] Decomposition.

Fig. 1. Typical temperature-time histories during combustion reaction under a N_2 pressure of 0.6 MPa with the composition of (A) B_2O_3: Mg=1:3, (B) B_2O_3: Mg: NaN_3=1:3:0.05 and (C) B_2O_3: Mg: NH_4Cl=1:3:0.1. (The insert shows the perforated aluminum container and the locations of thermocouples A and B.)