



Melt-assisted solid flame synthesis approach to amorphous boron nanoparticles



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ABSTRACT

A melt-assisted solid flame synthesis approach was applied to synthesize boron nanoparticles in argon gas and air atmospheres. For this purpose, we investigated the characteristics of a thermally induced combustion wave in $B_2O_3 + \alpha Mg$ mixtures ($\alpha = 1.0\text{--}1.5$ mol) in argon and air atmospheres. Utilizing stoichiometrically insufficient amounts of magnesium ensured that a large portion of molten B_2O_3 remained in the sample, which reduced the combustion parameters and favored the formation of boron nanoparticles. Under these conditions the combustion temperature and burning velocity were controlled in the range of 1300–1580 °C and 0.065–0.18 cm/s, respectively, and boron nanoparticles in a ~20–200 nm size range were obtained. The characteristics of boron nanoparticles (morphology, purity, specific surface area, oxidation activity, etc.) were analyzed and a reaction pathway leading to boron nanoparticles synthesis was proposed.

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1. Introduction

Over the past decades, there has been a consistent drive to improve the volumetric energy content of fuel to extend the flight distance of aerospace vehicles. High-energy fuel can provide more propulsion energy than conventional refined fuel and promote the flight range [1,2]. Up to now, using chemical synthesis, impressive progress has been made toward the development of high-energy liquid fuel [3,4]. An alternative to improve the energy content is the addition of energetic materials to the liquid fuel. Amorphous boron, because it has a high volumetric heat (135.8 MJ/L), is one of several candidates expected to improve the energy content of fuel [5]. Young et al. [6,7] evaluated the potential of boron particles as fuel additives for high-speed air breathing propulsion. Their results show that boron particles can be successfully ignited in an ethylene/oxygen pilot flame. Gan et al. [8] reported an improvement of the burning characteristics of nanofluid fuels (n-decane and ethanol) with the addition of boron nanoparticles.

However, the ignition and combustion of boron can be quite difficult due to its long ignition delay [9] and a naturally formed boron oxide liquid shell. This boron oxide layer inhibits the combustion process. Yuasa et al. [10] studied the effects of pressure and oxygen concentration on boron combustion and found that in air at 0.1 MPa the oxide layer melted at ~722 K before the boron core melted (~2350 K). A liquid oxide shell consequently forms around the solid boron core, and the combustion process is controlled by elemental boron diffusion through the liquid shell [11]. Therefore, different attempts have been made to improve the ignition and combustion characteristics of boron. One way to eliminate this liquid shell is vaporization; this strategy, however, is quite difficult because the boiling point of B_2O_3 is ~2316 K [12]. Another possible way to eliminate the shell is rupture, either by collision of the solid particles or through internal rupture. As the particle loading is typically low in combustor studies, there is little possibility for particles to collide. Ulas et al. [13] fluorinated the boron oxide shell with fluorine, which gave reduced burning times, but fluorine is toxic, thus preventing wide use of this method.

An effective alternative that can be used to enhance the ignition and combustion characteristics of amorphous boron is particle size reduction. Karmakar et al. [14] recently investigated the effects of particle size on the ignition and combustion behavior for two distinct size groups of boron nanoparticles. It was observed that the

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ignition delay was reduced for nano-sized particles, and they were completely oxidized in a swirl-type combustor at ~ 1773 K. Therefore, a number of approaches, such as arc decomposition of B_2H_6 [15], gas phase pyrolysis of $B_{10}H_{14}$ [16], gas phase reduction of BCl_3 in an inductively coupled plasma [17], solution reduction of BBr_3 with sodium naphthalenide [18], ball milling of coarse boron powder [19], and magnesiothermic reduction of freeze dried boron oxide at elevated temperatures [20] have been developed for the controlled synthesis of boron nanoparticles. The gas-phase and liquid synthesis methods [15–18] are associated with one or more disadvantages such as using expensive, extremely poisonous and inflammable reagents (B_2H_6 , $B_{10}H_{14}$, BCl_3 , BBr_3), complex work-up and purification, and generation of a large amount of toxic waste. The solid phase-synthesis approaches [19,20] have high energy consumption, long operating time, and may not produce boron nanoparticles of acceptable purity and size distribution. Therefore the development of simple, effective, unpolluted, and environmentally friendly approaches for B nanoparticles synthesis is therefore still a subject of intense investigation.

In our previous report [21] was focused on the synthesis of boron nanoparticles by heating a $B_2O_3 + 3Mg + kNaCl$ (k is the number of moles of NaCl) mixture in a laboratory oven at 800 °C under an argon flow. As prepared boron nanoparticles displayed good ignition characteristics, but some issues related to the synthesis process and boron purity still remained unresolved. The first of these is the energy consumption associated with preheating of the initial mixture to about 800 °C to start the combustion process. The second is the relatively large content of oxygen (from 4.5% to 50%) in the final boron nanoparticles, which negatively affects the volumetric energy content and combustion efficiency.

For these reasons, we researched an alternative approach that would enable the production of low oxygen content boron nanoparticles in less time and with no preheating procedure. We therefore modified the aforementioned composition of the initial mixture and conducted the combustion process at room temperature without any preheating. At first, NaCl in the initial mixture was replaced with alternative inorganic additives such as B_2O_3 , $Na_2B_4O_7$, or $MgCl_2$; second, the reaction pellet was ignited and combusted at room temperature, without preheating. With the new additives, a layer-by-layer and self-sustaining combustion process was realized. However, amorphous boron nanoparticles with acceptable particle sizes and purity were only obtained with B_2O_3 additive. Therefore, an initial mixture of $B_2O_3 + \alpha Mg$ ($0.8 \leq \alpha \leq 2.0$) composition was set for the basic experiments.

2. Experimental

The following chemicals were used to prepare the reaction samples: B_2O_3 (95% purity; particle size: 50–300 μm ; Daejung Chemical & Metal Co. Ltd., Korea) and Mg powder (98.5% purity; particle size: 50–200 μm ; Samchun Pure Chemicals, Co. Ltd., Korea). Experiments for producing boron nanopowder from a $B_2O_3 + \alpha Mg$ system for a $1.0 \leq \alpha \leq 1.5$ range (α is the mole number of Mg) in argon and air atmospheres were conducted. In a typical experiment a reaction mixture of 80–100 g prepared by hand mixing of raw materials in an agate mortar was hand-compacted into a quartz cup (diameter: 4.0–7.0 cm, height: 5–7 cm) (Fig. 1a). During compaction, two Λ -shaped tungsten-rhenium thermocouples (WR-26/WR-5), 100 μm in diameter (time constant ~ 0.05 s), were placed inside the sample near the center. Individual thermocouples were coated with a thin layer of Al_2O_3 (~ 5 – 10 μm) to increase their resistance to oxidation and to avoid possible interactions between the thermocouples and the powder bed at elevated temperatures. The upper thermocouple was placed ~ 2.0 cm from the top of the specimen and the thermocouples were fixed at a

distance of 2.5–3.0 cm from each other. Approximately 2–3 g of Ti + 0.9C (black soot) + 0.1[(C_2F_4) $_n$] was placed on top of the reaction sample as an ignition agent. A cup containing the reaction mixture and thermocouples was subsequently placed under a nickel/chromium coil in a combustion chamber. The chamber was then filled with argon, and the combustion process in gaseous argon was conducted at 0.1–1.0 MPa. Local ignition of the reaction sample was achieved within 1–2 s using a nickel–chromium filament that was electrically heated to 900–1000 °C (Fig. 1b). A computer-assisted data logger (GL100A, Graphtec Co., Japan) continuously recorded the millivolt–time history of the process at a rate of 10 Hz. The output voltage from the thermocouple was then converted to a usable temperature–time reading curvature using standard calibration curves for WR-26/WR-5 thermocouples. The combustion temperature was determined from the temperature profile by considering its maximum. The combustion velocity was calculated using $U_c = x/t$, where x is the distance between the thermocouples, and t is the time between the arrival of the front at each thermocouple. The locations of the thermocouples along the sample were also changed to assess the stability of the combustion wave along the sample. The uncertainty of the location of the thermocouples was $\sim 10\%$, which resulted in an identical uncertainty for the combustion velocities that were calculated from the thermocouple signals. The uncertainty of the temperature measured using the thermocouples was ± 10 – 15 °C or 2–5% of the measurement.

After completion of the combustion, the burnt sample was coarsely grinded and then transferred to a glass beaker for further purification. The reaction byproducts were removed by mixing the sample with concentrated HCl in a 500 mL glass beaker on a hot magnetic stir plate (Fig. 1c). The acid-leached powder was rinsed with distilled water and dried at 80–100 °C. A black-brownish and fluffy powder was obtained (Fig. 1d).

Thermodynamic calculations of the equilibrium concentration of all reaction species were performed using the commercially available software package “Thermo” (Russia, ISMAN) specially designed for combustion processes [22]. The amount of each phase was calculated as a function of temperature based on minimization of the Gibbs free energy. “Thermo” software does not account for the kinetics of the chemical reactions; it can therefore only approximate the actual system. However, the results enable rapid screening to identify the appropriate range for the reaction conditions that should be studied experimentally, thereby minimizing expensive trial-and-error chemistry.

The crystal structures and morphologies of the final powders were characterized using an X-ray diffractometer with $CuK\alpha$ radiation (Siemens D5000) and a high resolution field-emission scanning electron microscope (HR-FE-SEM, Hitachi S-4800). The specific surface area of the samples was determined using a SA-9600 Brunauer–Emmett–Teller (BET) surface area analyzer (Horiba). Raman scattering spectra were obtained at room temperature using a Horiba Jobin Yvon LABRAM-HR800 laser micro-Raman spectrometer with a 633 nm laser. Mg and B concentrations were evaluated by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo scientific iCAP 6500). A thermogravimetric analyzer (TGA/DSC-1, Mettler Toledo) was used to determine the oxidation behavior of the boron nanoparticles.

3. Results and discussion

3.1. Thermodynamic analysis and combustion experiments

The adiabatic combustion temperature (T_{ad}) and the equilibrium concentration of the reaction species for a $B_2O_3 + \alpha Mg$ (α is mole number of Mg) reaction system are shown in Fig. 2. In this

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