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Physicochemical properties of ball milled boron particles: Dry vs. wet ball milling process

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ABSTRACT

Physicochemical properties of both dry and wet milled boron particles with sub-micron sizes were investigated. Milling process was performed in N_2 atmosphere and the mass ratio of tungsten carbide ball and boron was fixed at 20:1. It was found that the size distribution of boron particles grinded under dry milling condition was much broader than that under wet milling condition, and the size reduction rate in the dry process was faster than that in the wet process. Dry milled boron particles showed rougher surface morphology and more agglomerated particles, compared to wet milled boron particles. On the basis of X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and FT-IR results, it was confirmed that the initial oxide layer on the surface of boron particles was removed in the wet milling process, and B–O–C bond was newly formed on the surface of boron. On the other hand, XRD results showed that crystalline boron oxide layer was formed on the surface of dry milled boron particles. In addition, appropriate cleaning cycles and drying time for wet milled boron particles were suggested on the basis of FT-IR data.

1. Introduction

Boron is an attractive material with applications in fuel additives [1,2], dopant in solar cell [3,4], and boron neutron capture therapy [5,6]. Especially, boron is a very interesting material as a fuel additive because it has high mass and volume specific combustion energy. The oxide layer on the surface of boron particle causes the problem of ignition time delay. As the particle size decreases, the mass fraction of pure boron decreases in terms of the single particle. Thus, the effect of oxide layer on the combustion performance of boron nanoparticles becomes significant [7]. Because the ignition time delay also lowers the combustion performance of micron sized boron particles, the removal of surface oxide layer on the boron particles and synthesis of metal coated boron particles have been studied to improve the combustion performance [8,9].

Boron particles can be synthesized by either bottom up [10–13] or top down [14–21] methods. As bottom up methods to produce boron particles, arc-pyrolysis of B_2H_6 [10], gas-phase pyrolysis of $B_{10}H_{14}$ [11], thermal plasma assisted decomposition of BCl_3 followed by a nucleation process [12], and the reduction of BBr_3 liquid using sodium naphthalenide [13] were investigated. As top down methods, milling [14], laser ablation [15] and dispersion by high pressure homogenizer [16] have been developed.

Among top down methods to fragmentize and process particles, milling processes have been the most widely used. The milling process can be operated under either dry or wet condition. Dry milling is performed by putting the ball and the boron feed in the milling jar [17,18]. In the dry milling process, typical parameters affecting the physico-chemical properties of particles are the type of milling equipment, milling energy, milling time, ball and powder ratio, particle rigidity and feed size. In the wet milling process, the properties of suspension such as viscosity, solid concentrate, and pH must be considered in addition to the properties of powder [14,19]. Using the ball milling process, various boron containing materials were synthesized. Boron carbide component that has lightweight and outstanding hardness was formed by high energy ball milling under dry condition [20]. The dry milling process was also used for the synthesis of other boron containing materials such as TiB_2 [21], and boron–titanium nanocomposite powders [22]. Boron powders were milled together with hydroxyl-terminated polybutadiene (HTPB) for the good dispersion of boron powder in fuel rich propellant under the wet milling condition [23].

As mentioned earlier, the boron oxide adversely affects the combustion performance. When the combustion of boron particle is initiated, the vaporization of oxide layer followed by heterogeneous reactions with oxidizer occurs on the surface of the boron particle. This process is very slow and takes up a large portion of the combustion time [24].

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In order to improve the combustion performance, the oxide layer on boron particles was removed [25] and the surface protected with energetic glycidyl azide polymer (GAP) [8] and metastable nanocomposite materials of boron particles with materials such as Ti and Zr [22] were used. There were several studies on the oxidation process and coating of nano-sized boron particles. The ambient oxidation of the as-produced boron nanoparticles synthesized with hypersonic plasma particle deposition (HPPD) system was also investigated [26]. From the study, it was found that the oxide layer is approximately 2 nm thick and a critical oxidation level was reached after approximately 2 days. Ball milling was used to produce similar to 50 nm particles, protected against room temperature oxidation by oleic acid functionalization [25]. Surface-functionalized boron particles with the formation of B – Br of B – O – R were synthesized [13]. Analysis method was proposed for the quantitative characterization of boron oxide and boric acid inside boron oxide layer [27].

Our study aims to provide the guideline for the selection of milling condition and milling process time for the control of particle morphology, size, and surface properties of sub-micron sized boron particles. In our study, we investigated physicochemical properties of ball milled sub-micron sized boron particles. Since milling process can significantly affect the particle shape, size distribution, and surface properties of boron particles, we compared the physicochemical properties of the ball milled boron particles under dry condition with those under wet condition in terms of particle size distribution, particle morphology, crystalline structure, and chemical composition. In addition, using Fourier transform infrared spectroscopy (FT-IR) optimized washing and drying processes for the post processing of wet milled particles were proposed.

2. Experimental

Boron particles were grinded under either dry or wet condition with a SPEX SamplePrep 8000M Mixer/Mill. In the dry milling process 2 g of boron powder (H.C. Starck, average size of 800 nm, purity of 95%) and 40 g of tungsten carbide balls (with diameter of 5 mm) were put into the milling jar. The milling jar was maintained in a nitrogen atmosphere using a glove box and vacuum packing to prevent the reaction between the surface of boron particles and oxygen in the atmosphere. A schematic diagram of the manufacturing process is shown in Fig. 1. During the process, boron particle samples were obtained by varying operation time from 2 to 4 h.

In the wet milling process, the boron powder and tungsten carbide ball were put into the milling jar as in the dry milling process. Also, 15 ml of anhydrous hexane (Sigma-Aldrich, purity of 95%) as a solvent and 1 ml of oleic acid (Sigma-Aldrich, USA) as a coating material were added to the milling jar. After the grinding process, cleaning and drying steps were additionally taken to remove physisorbed residues on the surface of boron particles and to make a powder form. Boron particles were washed by an ultrasonicator after the addition of methanol (Sigma-Aldrich, purity of 99.9%), and then were centrifuged at 3500 rpm for 10 min with a MF 80 (Hanil, Inc., Korea). In the drying process, washed samples were dried in an oven at 100 °C for 1 h or 2 h.

In order to obtain the physico-chemical properties of the ball milled boron particles, various characterization techniques were used. Scanning Electron Microscope (SEM) was used for the determination of the particle morphology of the milled boron particles. Energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectrometer (XPS) were used for the analysis of chemical composition and surface chemistry. Nanoparticle size analyzer (NPSA) was used to investigate the effects of milling condition and time on the particle size distribution. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to analyze the crystal structure of oxide layer on the boron surface. Fourier transform infrared spectroscopy (FT-IR) was used to demine the optimization condition of post processing on the wet milling process.

SEM images were obtained on a JEOL JSM-7000F operated at 0.5 to 30 kV beam energy and the EDS resolution of 133 eV. XPS measurements were performed on a MultiLab 2000 (Thermo Scientific, USA) equipped with a high performance Al K alpha X-ray source. The base pressure of the XPS system was 5×10^{-10} Torr. During the data collection the pressure equaled to ~5×10^{-9} Torr. The high resolution spectra were collected using 20 eV pass energy and 0.1 eV/step. The binding energies were referenced to the adventitious carbon 1 s peak at 284.5 eV. Nanoparticle size analyzer (NANOPHOX, Sympatec-GmbH Inc.) based on dynamic light scattering (also known as photon correlation spectroscopy) was used to obtain the size distribution of particles suspended in methanol solvent. The XRD patterns of milled boron particles were obtained in the 2 θ range from 5° to 70° with a D8 Advanced of Bruker AXS Inc. For TEM analysis, particles were fully dispersed with ethyl alcohol by ultrasonication. A few drops of the dispersion were deposited onto a lacey carbon grid for imaging. A FEI Technai G2 F30 TEM operating at 300 kV was used to obtain TEM images. FT-IR spectra between 600 and 4000 cm^{-1} were obtained by using a FT-IR spectrometer (FTS-175C, Bio-Rad-Laboratories Inc.) and spectra were scanned about 100 times.

3. Results and discussion

Fig. 2 shows SEM images of the un-milled, dry milled, and wet milled boron particles, respectively. Fig. 2(a) shows as-received boron particles with average size of 800 nm used in the present experiments. The average size was given in the specification sheet provided by the manufacturer. Fig. 2(b) and (c) shows dry and wet milled boron particles obtained after 1 h of milling, respectively. Bright and small spots shown in Fig. 2(b) and (c) represent tungsten carbide particles originated from the milling jar and ball. In comparison of Fig. 2(b) with (c), dry milled boron particles are shown to have rougher surface morphology and

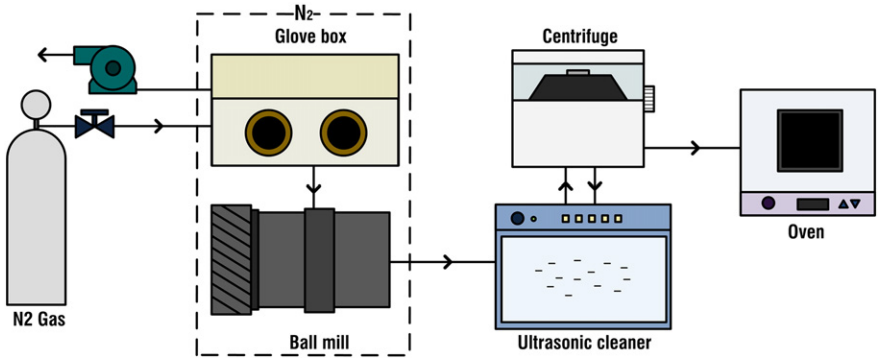

Fig. 1. Schematic diagram of dry and wet milling process.