Applied Surface Science 286 (2013) 91–98

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Enhanced reactivity of boron, through adding nano-aluminum and wet ball milling

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ARTICLE INFO

Article history:
Received 3 July 2013
Received in revised form 5 September 2013
Accepted 6 September 2013
Available online 14 September 2013

Keywords:
Boron powder
Nano-aluminum powder
Wet ball milling
SEM
TG–DSC

ABSTRACT

Boron is a significant component of energetic materials due to its high energy release on both a mass and volumetric basis. However, due to long-term exposure in air, boron is easily oxidized to form thick surface oxidation layer which significantly decreases the activity of boron. In this study, we demonstrate the wet high-energy milling method to purify the long-term storage boron and assemble the nanoaluminum and boron together to improve the activity of boron. The results show that after wet ball milling, the surface of boron particles becomes rough, and the aluminum is uniformly distributed on the surface of boron observed by scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS), respectively. Determined by simultaneous thermal analysis thermogravimetric–differential scanning calorimetric (TG–DSC) in oxygen, the heat release of boron is 444% higher than the boron without any processing. Combustion analyses of delay compositions consisting of boron powder with and without wet ball milling combined with barium dichromate were conducted to study the reactivity activity. The result shows that the average combustion rate for delay composition containing functionalization boron is 2.4 to 3.4 times than the others containing common boron. Overall, our work demonstrates that wet ball milling with adding nanoaluminum can be used an effective method to improve the reactivity activity of long-storage boron.

1. Introduction

Elemental boron has the advantages of high volumetric heat of combustion (140 kJ cm^{-3}) and gravimetric heat of combustion (59 kJ g^{-1}), these advantages make boron become a highly attractive fuel for rocket propellants and explosives, where being lightweight is paramount [1–6]. Despite the great potential of boron as a fuel, it has rarely achieved its potential in systems that require fast and complete combustion. The major reason is that the high melting point (2375 K) nature and the intrinsic oxide layer (B_2O_3) make the boron difficult to be ignited and completely combustion [7]. What is more, the oxide layer has a low melting point (718 K) and high boiling point (1773 K). When heated, the oxide shell will melt before the core. Then, the core will be totally coated by the liquid oxide layer which significantly impedes the contact between the core and the oxidizers. That significantly decreases the energy release productivity.

For long-term storage born powder, due to being exposed in air for a long time, it forms a thick oxide layer around the core of fuel [8]. Most recently many efforts have been made to address the issue of oxide layer removal. Many authors used solvent purification method and wet ball milling method [9] to improve the purification and activation of boron. Hui-xiang and Feng-qi [10] used ethanol and distilled water to soak the amorphous boron powder (purity:90%), implement the surface purification treatment of amorphous boron. Van Devener et al. [11] used the way of dry milling and wet milling to remove the oxide layer on the surface of boron powder, and the wet milling used *n*-hexane as a solvent. The results showed that after wet milling the solvent with oleic acid can effectively improve the activity of the boron powder.

In addition to the physical processing of boron, adding a small amount of combustible materials such as magnesium powder or aluminum powder [12] to the boron has also been widely used. PANG Wei-qiang et al. [13] added magnesium powder on the properties of boron (purity:90.05%)have been carried out relevant research and found that boron and magnesium composite powder used in the fuel-rich propellant was conducive to the improvement in fuel-rich combustion properties and burning rate pressure index. But there was seldom report about simply adding aluminum powder to the boron powder. In 2009, Sullivan et al. [14] used the pressurization rate inside a small combustion cell as a measurement of the reactivity. The results showed that the reaction of the aluminum powder (50 nm) and copper oxide (<50 nm) helped the ignition and combustion of the boron powder (62 nm).But

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http://dx.doi.org/10.1016/j.apsusc.2013.09.026

this phenomenon was not observed when micron boron was used instead.

Our previous work showed that compared with *n*-hexane, oleic acid and distilled water, pure ethanol had better effect to purify the long-term storage boron [15]. Here, we also choose the ethanol as the solvent in the wet milling process, and introduce the high-energy ball milling which can produce structural changes and chemical reactions by mechanical energy [16]. The aluminum nano particle was also added into micron boron. Al powder is easier to ignite than B powder, and B_2O_3 can react with Al, the products are boron and Al_2O_3. Hoping during combustion the Al can remove the liquid boron oxide. Thus the energy of boron powder can be completely released. We further investigated the combustion behavior of delay compounds comprising the treated boron with oxide and found the combustion performance had been significantly increased because of the wet ball milling.

2. Experimental Procedures

2.1. Sample preparation

Raw boron (B_O, amorphous, purity >97 wt%) was purchased from YingKou Pengda Fine Chemicals Co., Ltd (China). And the average particle size was 2 μm to 4 μm specified by the supplier. The boron was stored in brown glass bottle. The bottle was placed in desiccator for almost 10 years. After 10 years of storage, the purity might be less than 97 wt% due to the oxidation.

The aluminum powder (Al_0) purchased from Nanjing Emperor Nano Material Co., Ltd (China), and had an average primary particle diameter specified by the supplier to be 200 nm. Aluminum was packed in double poly bags vacuum.

In this study the wet high-energy milling method was used to purify the long-term storage boron. Pure ethanol (Sinopharm Chemical Reagent Co., Ltd.) was used as protective solution. It is helpful to prevent the further oxidation of boron and dissolve the B_2O_3.

In the process of ball milling, the size of the grinding ball, the material, the rotating speed, etc., all can produce certain effects on ball milling [17,18]. The type of mill we chose is planetary ball mill (ND7 frequency conversion planetary ball mill, Nanjing Tianzun electronics Co., Ltd (China)). The ball milling pot and materials of grinding balls in this experiment are agate, the diameter of jars is 7.5 cm, and the milling jars which internal volume are 250 ml. The size and quality of grinding ball which were used in the experiment of wet ball milling were shown in Table 1. The grinding balls were all used as long as the wet ball milling experiment happened, and kept the quality must be 150 g each time.

Table 1
The size of the grinding balls.

Size (mm)	Single quality (g)	Quantity
18	10	10
10	1.5	10
6	0.35	100

In the typical milling experiment, 5 g boron powder or 5 g boron/aluminum composite powder (mass ratio of boron to aluminum is 6:1) and 150 g (the charge ratio (mass ratio of ball to mass) was kept at 30:1) of milling balls as shown in Table 1 were loaded in the milling pot with 100 ml ethanol to help disperse the powder and prevent caking. The milling was conducted at 3 h and kept the rotate rate at 300 r/min. The obtained samples were centrifuged 10 min by using 7000 r/min centrifugal speed and then were dried in vacuum oven for 12 h at 70 °C. Finally, grinding dry samples were sieved by 80 mesh sieve. In this way we got the samples we need to do other characterization. In the whole article, we terms the boron as B_0 and B_1 for the sample before and after milling, the aluminum as Al_0 and Al_1 for the sample before and after milling, the boron/aluminum composition as $(B + Al)_0$ and $(B + Al)_1$ for the sample before and after milling. After preparation, the samples were packed in double poly bags vacuum.

2.2. Sample morphology analysis

Scanning electron microscopy (SEM) using Japanese Hitachi High-Technologies corporation production of S-4800II cold field emission high resolution scanning electron microscope (FESEM, accelerating voltage is 20 kV) to observe the morphology of the samples.

2.3. Thermal performance analysis

The thermal performances of the samples were investigated by means of TG–DSC (NETZSCH STA449C). All samples were placed in alumina crucibles (85 μl), weighted at 1 ± 0.05 mg, heating rate at 20 K/min from 40 °C to 1000 °C in the flowing stream of oxygen gas and the purge gas of high-purity argon with a gas flow rate of 20 ml/min.

2.4. Measurement of reactivity

In order to evaluate the activity of boron powder and boron/aluminum composite powder before and after milling,

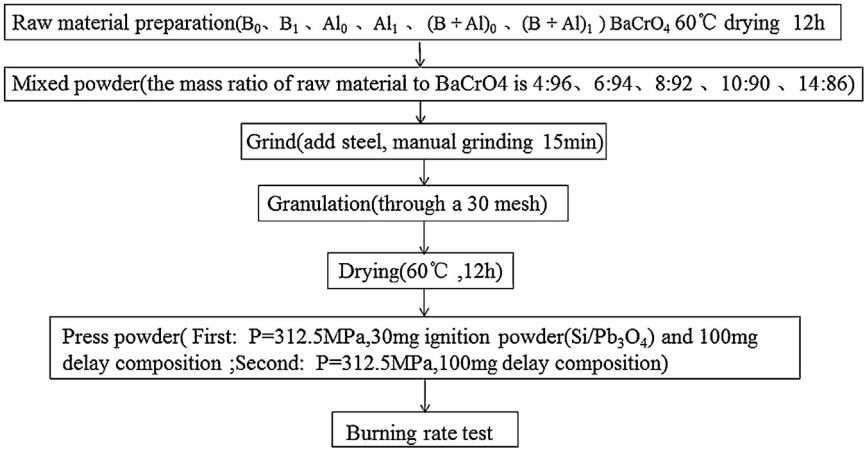

Fig. 1. The delay powder preparation process and burning rate test.