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Effect of metal hydrides on the burning characteristics of boron

Jianfei Xi, Jianzhong Liu, Yang Wang *, Daolun Liang, Junhu Zhou

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

In this study, the effect of four metal hydrides on the burning characteristics of boron was investigated. Thermogravimetric experiment results show that the thermal reaction process of boron samples can be divided into five stages. The thermal reactions of boron can be significantly promoted with LiH, which can reduce the initial temperature of the first violent reaction stage by ~140 °C. The starting temperature of the post-reaction stage also decreases by ~260 °C. The results of the laser ignition experiment suggest that all four metal hydrides can promote boron burning. Nonetheless, different metal hydrides display varied promotional effects. Among the studied hydrides, LiH is the most effective additive and shortens the ignition delay time of boron by ~34.1%. Moreover, it enhances the combustion intensity of boron by ~117.6%. The other three metal hydrides (CaH_2, TiH_2, and ZrH_2) can also contribute to boron burning.

1. Introduction

Elemental boron has long attracted interest as a fuel for propellants and explosives [1]. Among all chemical elements, boron has the highest volumetric heat of combustion (140 kJ/cm^3) and the third highest gravimetric heat of combustion (59 kJ/g^3) after H_2 and Be [2]. Although boron is exceptionally effective, its potential as a fuel or a fuel additive is yet to be realized partly because boron combustion is difficult to complete [3]. The external surface of most boron particles are coated with a layer of oxide film [4]. Boron ignition is thus hindered by this protective oxide layer, which liquefies at relatively low temperatures (450 °C at 0.1 MPa) and decelerates the effect of oxidizers on the underlying boron material [5]. Boron also has a high vaporization temperature (3727 °C at 0.1 MPa). The melting point of the oxide layer is much lower than that of the core boron particle (2077 °C at 0.1 MPa). On heating, the oxide shell on the boron particle melts before the solid core does, thus initiating a diffusion-controlled process through the molten shell [6]. Hence, numerous studies have aimed to promote boron ignition and combustion [7–9].

Spalding et al. [10] investigated the ignition of 24 micron boron particles in a shock tube at a pressure of 8.5 atm and temperature of 2500 K in atmospheres of pure O_2, 1% of SF_6 with 99% O_2, and 30% H_2O with 70% O_2. Data collected using emission spectroscopy and filtered photodiode detectors were presented. Wavelengths of BO and BO_2 emission corresponding to spectral features were observed in shock tube experiments. Emission form boron atoms or other molecules of interest, e.g., B_2O_3 and B_2O_2 is generally in the ultra-violet or infra-red and would not be observable with the present equipment. From the spectroscopic data collected, it was found that the dominant spectrum in the visible wavelength range during boron particle burning is that of the BO_2 molecule.

Liu et al. [11] studied the effect of boron particle coatings (LiF, Viton A, and silane) on the combustion of solid carrier propellants. The results indicate that the LiF-coated boron with propellant exhibits the most remarkable overall behavior. The propellant that contains LiF-coated boron particles has a shorter ignition time than that with Viton A-coated particles under similar heat fluxes. Under low fluxes, the ignition process is dominated by ammonium perchlorate (AP) decomposition and may shift to a condensed phase reaction under high heat fluxes.

Obuchi et al. [12] investigated the effect of magnalium as an ignition source on the ignition delay time and extent of combustion of boron. Ignition delay time was measured by an electronic furnace, and extent of combustion was obtained using a connected-pipe ducted rocket. As per their analysis, the ignition delay time of the mixture can be divided into two stages, namely, the early and late stages, unlike that of the boron particle (single stage). Boron mixed with magnalium can ignite at temperatures below that required for the ignition of boron alone. Therefore, the extent of combustion of a gas generator that contains boron can be improved by the addition of magnalium.

Mestwerdt et al. [13] studied the combustion characteristics of a boron/lithium mixture. An electrical resistance furnace with a graphite tube was used to run tests at temperatures higher than 1727 °C. Particle ignition and combustion were analyzed using

* Corresponding author. Tel.: +86 15669968110.
E-mail address: wy_coal@sina.com (Y. Wang).

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photographic equipment and spectrography. The results suggest that lithium additives can lower the ignition temperature of boron from 2227 °C to 527 °C (the mole ratio of boron/lithium was 2.5). The combination of boron and lithium lowers ignition temperature and completes the combustion process. The reaction is attributed to the lithium flame, which heated the particle to initiate the boron reaction.

To enhance boron ignition, various methods have been proposed, including [14,15]: (1) The ignition of boron particles in an environment with halogen; (2) the addition of metals, such as titanium and magnesium, to boron particles; (3) the coating of boron particles with energetic materials, including glycidyl azide polymer and AP; and (4) the coating of boron particles with materials that can react with boron oxide and remove the oxide layer, such as LiF and trimethylolpropane. Our team has also investigated the effect of several additives on the burning characteristics of boron, including combustible metals (Mg, Al, and Ti) [16], coating agents (AP and LiF) [17], and metal oxides (Bi_2O_3, Fe_2O_3, and SnO_2) [18]. All of these additives promote boron ignition and combustion in different degrees.

Some metals ignite more easily than boron. These metals act as ignition agents and promote boron burning when they are added to boron powders. Meanwhile, the evaporation rates of boron oxide can be enhanced by water vapor [4]. It also contributes to boron combustion. To generate these dual functions, we select some metal hydrides and determine their effect on the burning characteristics of boron powders. Thus far, no relevant study has been conducted.

Many metal hydrides have a high reactivity toward air and oxygen (like MgH_2, AlH_3) [19,20]. Given the actual application situation, we consider four stable metal hydrides, namely, lithium hydride (LiH), calcium hydride (CaH_2), titanium hydride (TiH_2), and zirconium hydride (ZrH_2). In this study, their effect on the burning characteristics of boron powders is systematically investigated. Furthermore, the thermal reaction characteristics of boron samples are identified using high-temperature thermobalance. The combustion characteristics of boron samples are also examined in a laser ignition facility. Specifically, we detect the influence of metal hydride addition on the ignition delay time and combustion intensity of boron.

2. Experimental

2.1. Materials

The boron particles (amorphous boron, purity 99.9%, particle size ~15.1 μm) used in our experiments were obtained from Baoding Zhongpuruituo Technology Co., Ltd. (China). Fig. 1 shows the scanning electron microscopy (SEM) image and the size distribution of the boron particles, which were composed of sub-micron-size boron regiments. In the boron particles, the amount of impurities was insufficient to affect their ignition and combustion behavior. The analytical-grade metal hydrides (10 μm–20 μm thick) used as the additives were purchased from Aladdin Industrial Corporation (China).

Given that boron is the main source of heat, limited amounts of metal hydrides should be added. In all experiments, we therefore applied an additive-to-boron ratio of 0.1 (on a weight basis). For each "metal hydride/boron" mixture, 2 g of boron and 0.2 g of metal hydride were placed in a mortar and properly blended with a pestle for 20 min. The resultant mixtures were denoted by $(LiH/B)_{0.1}$, $(CaH_2/B)_{0.1}$, $(TiH_2/B)_{0.1}$, and $(ZrH_2/B)_{0.1}$. Original boron was treated with the similar procedure as the control. The samples used in the experiment (original boron and "metal hydride/boron" mixtures) exhibited similar physical properties.

2.2. High-temperature thermobalance

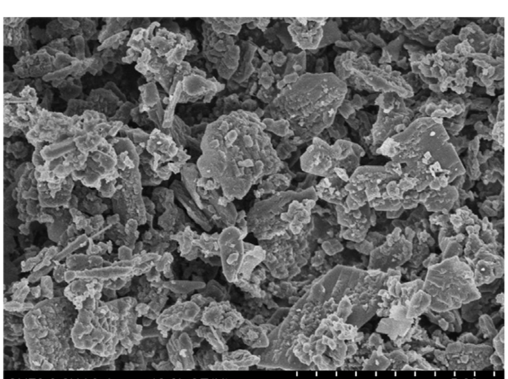
The thermal analysis experiments were conducted using a SETARAM Setsys Evolution thermobalance. We applied a heating rate of 20 °C/min and flow rate of 50 mL/min of 21 vol% O_2 in N_2. In each thermogravimetric (TG) experiment, we packed approximately 5 mg of the sample into the TG sample cup.

2.3. Laser ignition/combustion facility

In the ignition and combustion studies, we used a high-powered CO_2 laser that could generate 150 W in continuous-wave mode. During the laser ignition experiments, the boron samples (~30 mg) were ignited in static air. Fig. 2 depicts a representative scheme of the facility.

To generate a relatively intensive ignition source, a thin piece of transparent glass was used as a lens to focus the high power-density laser beam on the sample surface. The transparent quartz tube that contained the boron sample was placed into a crucible. The dynamic ignition and combustion behavior of the sample were recorded using a spectrometer, and the emitted spectrum effectively detected the initial and subsequent processes of boron combustion. The information detected by the spectrometer was recorded on a computer for further analysis.

The spectrometer was also used to determine the ignition delay time and combustion intensity of the boron samples. According to Li et al. [21] and Spalding et al. [22], the ignition and combustion of a boron particle generate a BO_2 molecule, which is a reactive



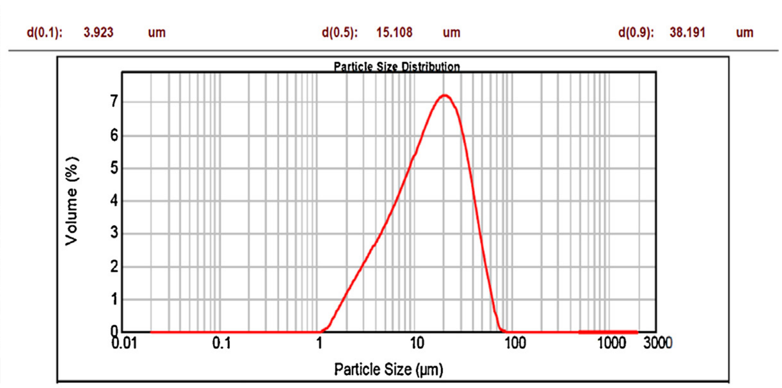


Fig. 1. SEM image (left) and size distribution (right) of boron particles.