



Enhanced ignition of milled boron-polytetrafluoroethylene mixtures

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ABSTRACT

The combustion and physical properties of boron-polytetrafluoroethylene (PTFE) mixtures were modified by ball milling. Examination of the milled material through optical microscopy, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) reveal that the milled mixtures are more intimately mixed and arranged into larger aggregate particles. Differential scanning calorimetry indicates the appearance of an endothermic reaction, brought on by milling. Fourier transform infrared spectroscopy provides evidence that the milling process enhances the chemical reaction of boron and PTFE. The milled boron-PTFE mixtures are demonstrated to be more reactive than those mixed by hand, despite containing larger particle sizes. Laser-ignition studies of the materials show that milling boron-PTFE mixtures results in the ignition delay times being reduced by a factor of 2. The milled mixtures were able to sustain combustion in air and emitted a strong BO_2 signal while simple physical mixtures do not. Enhanced reactivity of the milled materials is attributed to a combination of decreased diffusion lengths and disruption of the boron oxide shell during the milling process.

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1. Introduction

Boron is an attractive element for incorporation in energetic materials because it offers a good combination of high heating value and density. For reference, the volumetric heating value for elemental boron is 134.7 kJ/cm^3 , representing a 61% increase over aluminum, with a heating value of 83.9 kJ/cm^3 [1]. However, boron is not commonly used in propulsion applications and other energetic material applications due to some limitations. The primary limitations concern the ignition and complete combustion of boron particles. Boron has high melting and boiling points of 2349 K and 4200 K [2], respectively. In addition, boron particles have an oxide film that covers the outside of the particle preventing oxidizer and the boron fuel to diffuse towards each other for reactions to begin. This oxide coating has a low melting temperature (723 K) and in combustion causes adhesion or clumping of boron particles with melty exteriors. These agglomerates create larger particles that may not burn completely within the given residence time of a propulsion system. As a result, boron particles are difficult to ignite and sustain/complete combustion [3,4]. That being the case, boron particles require longer residence times than metal particles [5], and often boron requires the addition of combustion promoting compounds for self-sustained combustion studies [6]. The path to exploit the energy potential of boron for a combustion

environment is to enhance the ignition and decrease the combustion time [7,8].

Methods to accelerate boron combustion include using metals such as magnesium to raise the combustion temperature [1] or to change the reaction pathway with a combustion aid. Several studies have demonstrated that fluorocarbons including polytetrafluoroethylene (PTFE) accelerate boron combustion [9,10] and the combustion of metals such as aluminum [11]. In the case of boron, addition of fluorine and fluorine compounds has been found to result in exothermic boron oxide-PTFE (condensed phase) reactions that increase the combustion temperatures while eliminating the exposed boron oxide on the surface of the particles [12]. However, it has been reported that the presence of hydrofluoric acid actually increased boron particle ignition delay times in some instances [13,14].

For any combustion promotor, both the condensed phase and gas phase interaction should be examined to ensure boron reaction participation. Additives that increase the reaction temperature benefit boron combustion because higher temperature products favor complete combustion through formation of B_2O_3 rather than the relatively stable intermediate, HOBOR [15]. The boron oxide-fluorine-based reaction mechanism has been corroborated by results that indicate that fluorine addition enhances boron particle combustion in condensed-phase mixtures [16] while offering no benefit to boron oxide-free B_4C particles [17]. Although fluorine has been shown to increase boron particle burning times [18], the benefit of PTFE as a combustion aid for boron ignition has been demonstrated in a propulsion application that

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Table 1

Sample designations of the Boron PTFE mixtures are presented below.

Ball Milling Duration (minutes)	PTFE (wt.%, balance is boron)		
	7.5	15	30
0	PM1	PM2	PM3
15	MM1	MM2	MM3
30	MM4	MM4	MM6

investigated hybrid motors with pressed boron-PTFE fuel and N_2O as the oxidizer [19].

Further enhancement of metal combustion with combustion aids such as PTFE has been achieved through mechanical activation. Sippel et al. [20] demonstrated the enhancement of the ignition and combustion effect of PTFE on the aluminum by mechanical activation through ball milling. Enhancement was quantified by shifts in the endothermic or exothermic peaks using differential scanning calorimetry (DSC). Mechanical activation of boron with metals has also been shown to improve combustion performance [21,22].

The goal of the current study is to show that boron-PTFE reactivity can be significantly increased through ball milling. Enhanced reactivity, beyond the benefit of combining boron with a combustion aid, marks advancement in overcoming the traditionally high ignition temperature and slow combustion of amorphous boron particles.

2. Experimental techniques

2.1. Boron-PTFE mixture preparation

Fuel rich mixtures of boron-PTFE were prepared with 7.5 wt.%, 15 wt.%, and 30 wt.%, PTFE. Amorphous boron (H.C. Starck, PD-4031) was used in all mixtures with a mean particle size between 1–2 μm while the PTFE (Micro Powders, FLUO-300) had a mean diameter of 5–6 μm . High energy milled composite particles were produced in 20 g batches using a high energy ball mill (Retsch, EMAX). It should be noted that higher percentages of PTFE were also used in the high energy mill with little success although may not be useful for the application since additional PTFE will reduce the energy density. The lack of composite particle formation was attributed to the softness of the PTFE particles. The boron and PTFE particles were placed in 125 mL stainless steel grinding jars with 25 stainless steel balls measuring 10 mm in diameter as the milling media. The air-filled jars were loaded to a mass ratio of milling media to milled particles of 5:1. Milling times examined were 15 and 30 min. at a rotation speed of 1000 rpm. Temperature throughout the milling process was monitored by IR sensors within the mill that measure the temperature of the outer surface of the grinding jars. The highest temperature recorded during milling of the boron-PTFE powders was 46°C.

In all, 9 different boron-PTFE mixtures were prepared and will be discussed throughout this paper. Both the percentage PTFE and the milling times were varied. Table 1 describes all the samples prepared that will be examined in the sections that follow. It should be noted that the samples were not stable in lab air after milling at higher charge ratios (e.g. 10:1) or longer than 30 minutes. White gas was present after milling when the 125 mL container was opened. In the interest of safety, samples prepared here were not milled at higher charge ratios or for longer durations than 30 minutes. Thermal analysis revealed that the change in the ball-to-particle ratio did not significantly alter the response of the material.

2.2. Boron-PTFE mixture thermal and morphological analysis

Differences between the milled mixtures and physical mixtures were examined using SEM between 1000 and 10,000 times magnification, optical microscopy (Keyence, VH-S5), and EDS for both fluorine and boron maps. Small 3 mg samples of the boron-PTFE mixtures were analyzed using DSC. These samples were loaded into 40 μL aluminum pans for analysis in a Perkin Elmer DSC (DSC 8500). Both open and closed pan experiments were performed by flowing ultra-high purity nitrogen at 20 ml per minute. The heating rate was held constant at 20°C/min, beginning at 50°C and ending at 460°C.

All the mixtures listed in Table 1 were also examined using thermogravimetric/Fourier transform infrared analysis using a Nicolet Nexus 870 FTIR spectrometer and a TA instruments Q50 TGA. The instruments were linked by a heated cell and transfer line, both maintained at 150°C. The FTIR spectra were recorded at a 4 cm^{-1} resolution; each spectrum used for analysis was an average of 32 scans at a collection rate of 1 Hz. All spectra were background subtracted and baseline corrected. The TGA was set to heat the samples, all with an initial mass between 5 and 10 mg, from room temperature up to 650°C at a rate of 20°C/min with mass measured at a frequency of 2 Hz.

2.3. Combustion and Ignition Experiments

Measurements of the ignition delay of boron-PTFE mixtures were made by igniting the mixtures detailed in Table 1 using a CO_2 laser system. The laser (Coherent, Diamond E-series 400) was calibrated to a flux levels of 120, 200, 350 W/cm^2 using a thermopile sensor (Newport 818P-500-55, Coherent Fieldmate). Laser energy, with a Gaussian beam profile, was directed onto a small crucible, with an area of 7.1 mm^2 of lightly tamped boron-PTFE mixture. The laser duration was set to times as long as 1 second, and first light was monitored using a high-speed camera (Photron SA1.1) mated to a long distance microscopic lens (Infinity, K2). In addition to a high speed camera, an Ocean Optics spectrometer (HR4000-ER) was integrated to observe any optical emission in the ultraviolet-visible-near infrared portions of the spectrum. Ignition delay was defined as the time between first exposure of the powder to laser energy and appearance of first light in the high speed recording, to the nearest 0.4 ms–1.0 ms, depending on the frame rate. The high-speed camera recorded at least three ignition events and ensuing combustion at 1000–2500 fps for each mixture detailed in Table 1. Exposure times were varied between 1 ms and 1.05 μs to capture the flame zone and particle dynamics within the reaction.

3. Results and discussion

3.1. Milled Boron-PTFE physical changes

The high energy ball milling process was found to alter the morphology of the physical mixtures. The physical mixtures (PM1–3) all had a similar appearance in SEM images, characterized by clumps of agglomerated fine particles. An example of this morphology can be seen in Fig. 1A below. After milling, the principal observed difference was the presence of larger, rounded particles. The reader is encouraged to compare Figs. 1A and B to note the effect of milling. A closer look at the particles under the SEM revealed that they are tightly packed agglomerates of boron particles with PTFE acting like a filler or adhesive that binds them together (Fig. 1C). In some instances, the PTFE appeared to have a web structure indicating the PTFE had deformed (see the lower right hand side of Fig. 1C). The milling process examined here, with such as disparity in hardness between boron (4900 MPa Vickers hardness) and PTFE (5.8–7 MPa) [23], can be thought of as repeatedly

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