



Oxidation kinetics and combustion of boron particles with modified surface



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ABSTRACT

This work is aimed to modify a commercial 95% pure boron powder to improve its ignition. The powder is processed using acetonitrile to dissolve the oxidized and hydrated surface layers. The washed powder re-oxidizes and agglomerates readily, which can be prevented by additionally washing it in toluene and other liquid hydrocarbons, prior to exposing it to an oxidizing atmosphere. The presence and removal of the hydrated oxide layer and oxidation of boron powders are studied using thermo-gravimetry. The processed powders are shown to retain the active boron present in the starting material and maintain their reactivity after extended exposure to an oxidizing environment. The powders are also injected in a pre-mixed air-acetylene flame and their ignition and combustion are studied based on their optical emission. Flame temperature is measured using optical emission spectroscopy. Powder particles washed in acetonitrile, toluene and hexane exhibit substantially shorter ignition delays compared to the starting commercial boron particles. Full-fledged combustion is unaffected by this processing: both, burn times and flame temperatures are nearly identical for commercial and modified powder particles.

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1. Introduction

Boron is an attractive material for metal combustion applications, such as explosives [1] and solid fuel additives for rocket propellants [2], because of its high gravimetric and volumetric heats of oxidation [3]. However, its long ignition delays [4,5] and extended combustion times [6,7] present major challenges for its practical use.

There have been considerable experimental and theoretical efforts [6,8–14] to understand and characterize the oxidation kinetics and combustion mechanism of boron. Specific focus was on long ignition delays [7,15]. It has been generally agreed that a natural surface layer of oxide (B_2O_3) or hydroxide (approximately 0.5 nm [16]) inhibits boron oxidation and therefore delays ignition [2], which leads to reduced bulk burn rates.

An accelerated removal of the boron oxide layer is expected to lead to shorter ignition delays, motivating multiple relevant efforts, e.g., see review [17]. Different studies considered addition of coating agents [18], metals [19], metal anhydrides or oxides [8,20–24], rare-earth metal catalysts [21], polymers and fluorinated compounds [2,25,26].

Experiments [21] showed that for boron nanoparticles ball milled with ceria (20 wt%) ignition delays were reduced by almost

a factor of 6. This was based on chemiluminescence measurements at a wavelength of 546 nm for particles fed in the combustion products of an ethanol flame in a customized combustor. Unfortunately, including 20 wt% of an oxide substantially reduces the energy density of an energetic composition.

The effects of metal hydrides (Ca, Li, Ti and Zr) on the ignition and combustion of 99% boron particles in a CO_2 laser were studied in Ref. [24]. Results indicated that the lithium hydride blended with a mass ratio of 10:1 in favor of boron, reduced ignition delays from 140 ms to as low as 90 ms. However, lithium hydride is difficult to handle and make compatible with processes involved with preparation of energetic formulations.

Adding fluorinated compounds or working with fluorine-containing gaseous oxidizers was shown to improve boron combustion and reduce ignition delay times, which was associated with alternate reaction pathways [2]. Practical introduction of fluorine in the reactive material may be difficult. Ignition of mixed polytetrafluoroethylene (PTFE)/boron systems was considered in Ref. [26]. It was concluded that for thermodynamically attractive, boron-rich compositions, adding PTFE was ineffective for promoting ignition.

Ignition of mixed boron and magnesium powders was analyzed in Refs. [19,27]. Selective ignition of magnesium occurred independently of the composition; it remained unclear whether ignition of magnesium was effective in igniting boron. Another approach to modifying ignition behavior of boron was proposed in Ref. [28], where the boron surface was coated with a carbide layer. The

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Table 1
List of materials prepared for investigation.

Sample ID	Starting material	Washing cycles		
		In acetonitrile, 3	In toluene, 5	In hexane, 3
A	95% pure boron	No	No	No
B	95% pure boron	Yes	No	No
C	95% pure boron	Yes	Yes	No
D	95% pure boron	Yes	Yes	Yes
E	99% pure boron	No	No	No

coating was formed by prolonged exposure of boron particles to hydrocarbons at elevated temperatures. However, X-ray photoelectron spectroscopy showed that the surface layer was substantially oxidized, and that the carbide surface layer was unfavorable for rapid ignition and heat release of the sample.

Generally, a challenge with most boron additives or coatings is that they reduce the overall material energy density. Significant kinetic effects accelerating removal of the boron oxide are observed with substantial amounts of such added components, and thus, materials with significantly reduced heats of combustion. The objective of this effort is to reduce boron particle ignition delays without imposing an energetic penalty associated with most additives. The approach here is to dissolve the natural boron oxide or boric acid layer from the particle surface while preventing the powder from rapid re-oxidation.

2. Experimental section

2.1. Materials

Commonly, boron powders are coated with a surface layer of boron oxide, B_2O_3 , which readily converts into boric acid, $B(OH)_3$, in humid environments [29]. Reported data on solubility of boron oxide are scarce, while boric acid can be dissolved in many solvents, most easily in water and ethanol [30]. However, most effective solvents contain oxygen and thus may oxidize the exposed boron surface. To avoid such oxidation, an oxygen-free polar solvent, acetonitrile, was considered in this work. No literature data on solubility of boron oxide or boric acid in acetonitrile were found. Therefore, solubility of boron oxide in acetonitrile was investigated preliminarily. Alfa Aesar acetonitrile 99.5% was used. A 2.5-g batch of 99.98% commercial boron oxide by Alfa Aesar was placed in a beaker with 30 mL of acetonitrile at room temperature and agitated by a magnetic stirrer for 10 min. The suspension was allowed to settle for 1 h. The clear liquid was siphoned from the top and centrifuged. The weight of the solid precipitated from the obtained clear solution was then determined. The solubility of boron oxide in acetonitrile was found to be 30 g/L. The precipitate obtained in room air with about 70% humidity had characteristic crystal structure of boric acid. Similar experiments with Alfa Aesar 95% n-hexanes and ChemPUR® commercial grade toluene showed that less than 0.1 g/L of solid could be recovered. These preliminary experiments guided preparation of modified boron samples, as discussed below.

All boron samples used in experiments are described in Table 1. Sample A, an amorphous boron powder, 95 wt% pure from SB Boron was used as both the reference and starting material. Sample E, a crystalline boron powder with 99 wt% purity, by Alfa Aesar was used as an additional reference material. Samples B, C, and D were obtained starting with sample A and using washing cycles aimed to remove or minimize the thickness of the natural boron oxide or boric acid layer. 10 grams of the starting powder were loaded into a 50 mL steel vial of a SPEX Certiprep 8000 series shaker mill with 30 mL of acetonitrile. The mixture was shaken for 30 min with no milling media. The sample was allowed to settle, and the acetonitrile was siphoned off without exposing

the washed boron to air. To rinse the washed boron, fresh acetonitrile was added, and the sample was vigorously stirred using Scientific Industries Inc. Vortex Genie X4674 shaker. Using an LW Scientific Ultra 8F-1 centrifuge, the acetonitrile solution was then separated from the boron powder and siphoned off. This cycle was repeated three times. After the third cycle, toluene was added, and the material was rinsed with toluene five more times. Some samples were additionally rinsed three times with hexane. After preparation, samples remained stored in the solvent used in their respective last washing cycle. Table 1 lists different materials prepared and compared in this study.

The prepared samples were characterized using laser scattering, optical and scanning electron microscopic (SEM) techniques. Images of the prepared samples A, B, C, and D obtained using a LEO 1530 field emission SEM are shown in Fig. 1. Sample B washed in acetonitrile only consists of strongly agglomerated particles. There are large crystalline formations consistent with precipitates of oxides remaining after rinsing with acetonitrile only. This is indicative of incomplete removal of the solvent, and this material was, therefore, not used in further experiments. Particle shapes and agglomerate morphologies observed for as received boron, sample A, and both samples C and D, finally processed using toluene and hexane, respectively are essentially the same. Note, however, that the sizes of agglomerates in samples C and D are somewhat greater than those in sample A.

Particle sizes were analyzed for samples A, C, and D, using SEM images of particles fed into the burner used in the combustion experiments (see below). The powder exiting from the burner was collected for fifteen seconds on a 1-kV charged aluminum surface positioned 4 cm above the burner to enhance collection of fine particles electrophoretically. SEM image processing enabled us to account for agglomeration and fractal dimension [31] of the actual particles fed into the flame. Images were collected at different magnifications. For each magnification, the images were processed to identify particles and to measure their sizes using ImageJ, a freely available software package by the National Institute of Health. The size distributions were then constructed using all recorded images. The equivalent particle diameters were measured and corrected by the agglomerate fractal dimension (FD), determined using the box counting method [32]. The FD value was approximately 1.8 for all materials. For additional details describing how particle size distributions are obtained from SEM image processing see Ref. [31]. The resulting particle size distributions are shown in Fig. 2. Preparing the samples to account for agglomeration shifts the distributions towards larger sizes. It is also observed that washed samples C and D are somewhat more agglomerated compared to the commercial powder A. This is consistent with qualitative observation made while examining the obtained SEM images shown in Fig. 1. These size distributions were correlated with the measured burn times and ignition delays.

2.2. Particle combustion experiments

Aerosolized particles were injected in an air-acetylene flame. Particle emission streaks were photographed. The locations where streaks were observed to originate were treated as locations where particles ignited; thus, ignition delays were obtained accounting for the injected particle velocities calculated for the experimental flow conditions. Particle burn times and temperatures were obtained from the optical emission measurements. Both, burn times and ignition delays were correlated with the measured particle size distributions.

The experimental setup is shown schematically in Fig. 3; it has been described in detail elsewhere [9,33,34]. The particles entered the flame through a brass tube with 2.39 mm internal diameter, placed axially at the center of the burner's nozzle. Pre-mixed air

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