



Boron-based reactive materials with high concentrations of iodine as a biocidal additive



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HIGHLIGHTS

- Up to 30 wt% of iodine is stabilized in boron mechanochemically.
- Main iodine release occurs upon heating above 400 °C.
- Boron-iodine milled with $\text{Ca}(\text{IO}_3)_2$ to prepare thermite containing up to 57.6 wt% of iodine.
- Thermite agglomerates burn at 2050 K releasing gas and fine oxide particles as products.

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ABSTRACT

Metal-based iodine-bearing reactive materials are of interest as additives to energetic formulations aimed to defeat biological weapons of mass destruction. This work was aimed to develop a material including a boron-based thermite with the maximized iodine concentration. The thermite was prepared mechanochemically, and $\text{Ca}(\text{IO}_3)_2$ served as an oxidizer. First, a B-I₂ composite powder was prepared starting with 40 wt% of iodine. This composite retains up to 30% of iodine, which is released in three steps upon heating. The main iodine loss occurs at temperatures exceeding 673 K (400 °C). The binary B-I₂ powder was used as a starting material to prepare the final thermite with the total concentration of iodine of 57.6 wt%. The thermite comprises loose agglomerates with particle sizes in the range of 1–10 μm, with submicron boron-iodine particles embedded in $\text{Ca}(\text{IO}_3)_2$. Combustion tests of the ternary composite thermite powder in an air-acetylene flame showed the flame temperatures close to 2050 K, and solid residue in the form of fine oxidized spheres with boron and calcium oxides mixed homogeneously. A correlation between particle sizes and their burn times is reported as well.

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1. Introduction

Specialized agent-defeat munitions are needed to neutralize stockpiles of chemical and biological weapons [1]. Bio-agent defeat often relies on halogens. In particular, compositions releasing iodine have been explored recently [2,3]. Metals are included in explosives to increase their energy density, and thus reactive materials combining highly exothermic metallic fuels with iodine have been studied as potential components of advanced explosive formulations, e.g., [4–8]. Although such materials must be stable at room temperature and easy to handle, they should burn rapidly and release copious amounts of iodine in order to be of practical interest [9].

Previous research showed that iodine could be mechanochemically stabilized in metal-based powders [6,7,10–12]. It was found

that up to 20 wt% of iodine can be stabilized in aluminum. Both, binary Al-I₂ and ternary composites, e.g., Al-B-I₂, containing 20 wt % of iodine were described and characterized. Kinetics of iodine release upon heating a ternary Al-B-I₂ composite suggests that iodine can be partially retained in both aluminum and boron [12]. However, the maximum concentration of iodine that can be retained in a mechanochemically prepared binary B-I₂ composite was not established.

In addition to including iodine as a component of a metal fuel, iodine can be effectively included in reactive materials as part of an oxidizer. For example, extensive studies addressed thermites using I₂O₅ as an oxidizer [13–16]. While very reactive, this oxidizer is also hygroscopic and thus is difficult to handle in ambient air. Other iodine-rich oxidizers were suggested [17–19], some of which, e.g., calcium iodate, $\text{Ca}(\text{IO}_3)_2$, are more stable and easier to work with than iodine pentoxide [20]. Recently, thermite samples combining commercial aluminum or boron with $\text{Ca}(\text{IO}_3)_2$ were prepared and characterized [21].

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This work is aimed to determine the maximum iodine concentration that can be retained in a binary, B-I₂ composite, and to combine such a composite with a stable, iodine rich oxidizer Ca(IO₃)₂ to prepare an energetic composition with the maximized iodine concentration.

2. Materials and experimental techniques

A commercial 95-% pure amorphous boron powder by SB Boron was used in this work to prepare all boron-iodine composite materials. For some samples, it was preliminarily functionalized by washing it in acetonitrile (99.5% pure by Alfa Aesar), generally following the methodology described elsewhere [22]. This processing removes B(OH)₃ and partially dissolves B₂O₃ from the powder particle surfaces. To enhance washing, the suspension of boron in acetonitrile was ultrasonicated using a titanium horn powered by a 20-kHz Branson 910BC system following the procedure established recently [23]. The suspension stratified, with the bottom layer representing the cleanest boron, which was loosely agglomerated. The material from the bottom layer was separated and dried in argon. This processed powder has its particle surface functionalized as a result of reaction with acetonitrile, protecting the powder from rapid re-oxidation upon its exposure to room air [23].

Both, as-received and functionalized boron powders were further milled with iodine (99% pure chips from Sigma Aldrich) in a shaker mill (SM) by SPEX Certiprep, 8000 series. For reference experiments, a commercial boron oxide (99.98% pure by Alfa Aesar) was also milled with iodine. Milling experiments used flat-ended steel vials and 3/8" (9.5 mm) diameter carbon steel balls. Each vial contained 5 g of powder and 50 g of balls, so that the ball to powder mass ratio (BPR) was set to 10. No process control agent was added. Compositions with the initial concentrations of iodine of 30, 40, and 50 wt% were prepared. The milling times were set to 2, 4, and 6 h. Milling vials were sealed in a glovebox under argon before milling. The vials with milling products were also opened in the same glovebox. The recovered powder was stored in closed but not sealed glass bottles. A list of the prepared binary boron-iodine samples with their respective milling conditions is given in Table 1.

Following characterization of the samples described in Table 1 (see results below), C-B₆₀I₄₀-4 was selected as the most promising binary material. It was combined with Ca(IO₃)₂ (98% pure, from Sigma Aldrich) to prepare a thermite. The thermite was prepared by milling the starting components for 1 h in custom-made high-pressure vials using a planetary mill (Retsch PM-400 MA). Each powder batch contained 21.6 g of Ca(IO₃)₂ and 8.4 g of C-B₆₀I₄₀-4, yielding product with a total of 57.6 wt% of iodine. This thermite composition has an equivalence ratio of 2.24 (B:Ca(IO₃)₂). The BPR was set to 10; the same steel balls as described above were used. In each vial, 15 mL of n-hexane (95% pure from Alfa Aesar) was used as a process control agent. As before, the milling vials were sealed and opened inside an argon-filled glovebox. Prepared thermite powders were dried and stored in glass vials.

Table 1
Prepared boron-iodine composite samples.

Sample Identifier	Boron	Iodine concentration, wt%	Milling times, hr
C-B ₇₀ I ₃₀ -4	Commercial	30	4
C-B ₆₀ I ₄₀ -2	Commercial	40	2
C-B ₆₀ I ₄₀ -4	Commercial	40	4
C-B ₆₀ I ₄₀ -6	Commercial	40	6
C-B ₅₀ I ₅₀ -6	Commercial	50	6
F-B ₇₀ I ₃₀ -4	Functionalized (washed in acetonitrile)	30	4
F-B ₆₀ I ₄₀ -4	Functionalized (washed in acetonitrile)	40	4
B ₂ O ₃ B ₆₀ I ₄₀ -4	Commercial ^a	40	4

^a Commercial B₂O₃ was used instead of Boron.

Thermo-gravimetric (TG) analysis was used to test the stability of binary boron-iodine materials using a TA instrument model Q5000IR analyzer. The samples were heated to 900 °C in argon at a rate of 5 °C/min. The purge flow of argon was 10 mL/min, and sample flow of argon was 20 mL/min. No TG measurements were performed for thermite samples to minimize the contamination of the furnace with highly corrosive iodine vapors.

Prepared thermite powders were examined using a LEO 1530 Field Emission Scanning Electron Microscope (SEM). SEM images were used to obtain particle size distributions of the prepared thermites, necessary for interpretation of combustion experiments.

A 532 nm Thermo Fisher Scientific DXR Raman Microscope was used to detect the surface molecular structure and composition of boron-iodine materials.

Combustion of thermite particles was studied by injecting them into an air-acetylene flame, following the methodology described in detail elsewhere [24,25]. Powder samples were loaded on a screw feeder and injected axially into a premixed flame using nitrogen carrier gas. The gas flow rate of nitrogen was 2 standard cubic feet per hour (SCFH). The powder entered the flame through a 2.38-mm diameter tube at a speed of 6 m/s. The premixed flame was obtained combining compressed air fed at 10 SCFH and acetylene fed at 0.9 SCFH. The equivalence ratio of the flame was 1.65. Optical emission of the burning particles was captured using a photomultiplier tube (PMT, Hamamatsu model R3896-03) equipped with a 700-nm interference filter. The pulse durations recorded by the PMT were interpreted as particle burn times. The distribution of the measured particle burn times was correlated with the measured particle size distribution to determine the effect of particle size on its burn time. In addition, the time-resolved spectra were captured using a 32-channel multianode PMT, Hamamatsu model H7260, coupled with a spectrometer covering the wavelength range of 430–641 nm. The spectra were used to evaluate the temperature histories of the burning thermite particles.

Ignition of the prepared thermite was measured using an electrically heated filament. The details of the setup are described elsewhere [26,27]. The sample was mixed with hexane and coated as a slurry on a nickel-chromium wire. After hexane dried, the wire was heated electrically by a DC current. Heating rates varied from 1500 to 30,000 K/s. The wire temperature was measured in real time by an infrared pyrometer. The ignition of the powder coating was captured using a high-speed camera (MotionPro500 by Redlake) operated at 500 fps. The filament temperature at the ignition instant was treated as the powder ignition temperature.

3. Results

3.1. Binary boron-iodine materials

Preliminary TG experiments addressed the effect of milling time on iodine stabilization in boron. In addition, a possible interaction between B₂O₃ and iodine in the composite material was addressed replacing boron with boron oxide as a starting component. The

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