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Combustion of sonochemically-generated Ti—Al—B nanopowders in a premixed methane/air dust flame

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ABSTRACT

Sonochemically-generated Ti—Al—B reactive mixed-metal nanopowders were tested by seeding them into a premixed, fuel-lean ($\Phi = 0.63$), methane/air flame to investigate their combustion characteristics. Tests were conducted on powders with and without cryogenic milling. The attenuation of a diode laser beam was measured to calculate the time-resolved concentration of the powder in the flame. Radiant heat flux was measured with three gauges at different heights (1 cm, 6 cm, and 12 cm) along the axis of the flame. Flame spectra were collected to monitor chemiluminescence of intermediate species, and a multi-wavelength pyrometry method was applied to the spectra to calculate the temperature of the hot particulates in the flame. Commercially available metal powders were tested as a benchmark. These included micron-scale aluminum, nano-scale aluminum, micron-scale boron, and inert nano-scale alumina powders. The spectra from flames seeded with the sonochemically-generated Ti—Al—B powder show strong chemiluminescence from the BO_2, an indicator of boron oxidation. Peak temperatures measured with flame pyrometry were approximately 2100 K, which is below the vaporization point of B_2O_3. The radiant heat flux from the seeded flame increased with concentration faster for the Ti—Al—B material than for any of the commercial powders, suggesting a greater gravimetric power density. Based on these results, the Ti—Al—B powders show promising combustion and heat-release characteristics, and therefore warrant further examination as a high-performance solid fuel.

1. Introduction

Metal and metalloid solid-fuel additives can significantly boost the volumetric energy density of fuels. Elemental boron has the highest theoretical volumetric heat of combustion of any fuel, as the oxidation reaction to form solid B_2O_3 results in the release of 137.7 kJ/cm^3 of boron, a volumetric energy density roughly four times that of liquid jet fuel. Boron is difficult to ignite, and pure boron combustion, especially in the presence of hydrogen, has significant technical challenges [1–3]. Boron's high theoretical heat release has yet to be realized in a system useful for current propulsion or energy-generation technology. The highly refractory nature of boron limits the rate of oxidation in two significant ways. Firstly, because the melting point of boron (2349 K) is significantly higher than that of B_2O_3 (723 K), the molten oxide layer on boron particles effectively coats the metallic core and prevents ignition until the particle is heated above the oxide boiling point (1770 K). Secondly, the high boiling point of boron (4200 K) prevents it from ever gasifying during combustion. Therefore, combustion is kinetically limited by heterogeneous reactions at the boron surface, resulting in relatively slow energy release rates. In addition, HOBO, the thermodynamically favored product when hydrogen is available at high temperature, remains kinetically stable in the gas phase until very low temperature [1–3]. Recent research has been published on the use of nanometer-sized boron (nm-B) [4–7] to overcome the aforementioned difficulties with boron combustion. The use of fluorine as an oxidizer has also been studied to avoid such issues [8,9]. Our approach to overcoming these difficulties is the use of a custom reactive metal powder where the boron is intimately mixed with hydrogen and metals having more favorable combustion properties.

Previously, we developed wet sonochemical techniques to produce amorphous reactive metal nanopowders (RMNPs) that enable the incorporation of atomically dispersed multiple reactive metals, as well as carbon and hydrogen, in a nanopowder fuel [10–15]. Boron-containing RMNPs that also contain titanium and aluminum were recently reported and proposed as a novel approach toward realizing the energy of boron oxidation for practical applications [14]. Our reactive powders are generated via the reaction of a group 4 transition metal halide and lithium metal hydrides in a relatively inert solvent (alkane or ether) and agitated

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with a benchtop ultrasound bath. This is followed by purification and thermal treatment to yield optimized RMNPs with high energy content [11,13]. An additional attractive feature of these powders as fuels is that they can contain as much as 20 molar percent hydrogen. Powders generated using a mixture of $TiCl_4$, $LiAlH_4$, and $LiBH_4$ were found to contain as much as 34 kJ/g in oxygen bomb calorimetry measurements [14]. Although this is significantly lower than the theoretical heat of combustion for boron (58.9 kJ/g), it is 59% greater than the measured heat of combustion from commercial nm-B (19.9 kJ/g) [14].

The objective of the current study is to gain insight into the combustion characteristics associated with these powders when they are reacting in a hydrocarbon flame. To accomplish this, we studied the reaction of RMNPs seeded into a fuel-lean, premixed, methane-air flame, to simulate its behavior in a combustor. For purposes of comparison, commercially available powders of micrometer-sized aluminum (µm-Al), nanometer-sized aluminum (nm-Al), nanometer-sized aluminum oxide (nm-Al_2O_3), and micrometer-sized boron (µm-B) were also tested to provide further insight into the combustion processes. The work herein focuses on the reaction of RMNPs entrained in a fuel-lean mixture of methane and air at atmospheric pressure and how it compares with commercially-available, single-metal solid fuels. Reactive metal powders of aluminum, the most common metal powder fuel, have previously been studied in multiple contexts, including as combusting dust, to help understand industrial safety issues as well as for their performance as fuels for solid rocket propellants and explosives. The combustion of µm-Al particles is relatively well understood [16], and powders comprising µm-Al particles have been studied as combusting dust clouds in propagating and stationary flames [17–19]. The fundamental study of metal combustion has generally focused on the mechanism associated with the combustion of a single, isolated particle, and the literature examining dust flames has shown this approach is insufficient for understanding how heavily metalized flames will behave. Therefore, we have undertaken the approach of examining metal powder combustion within the framework of a full flame system.

The proliferation of nanopowders has prompted more recent investigations into the ignition and propagation of reactions in nm-Al dust clouds. For very small particles, theory predicts that the time scales for mass diffusion will be much shorter than the time scales for reaction, leading to combustion that is ‘kinetically-controlled’ [20]. Studies have shown that the burning time for nm-Al shows a strong dependence on the ambient temperature and pressure, suggesting that the combustion is in the kinetically-controlled regime [21]. The minimum ignition energy of aluminum powder with an average particle diameter of 100 nm is less than 1 mJ, an order of magnitude lower than that of µm-Al powders [22]. Huang et al. studied bimodal powders of nm-Al and µm-Al particles in a stationary aerosol flame and found that higher concentrations of nanoparticles increased flame speeds; however, the flame zone thickness was significantly increased and luminosity was decreased [23].

In this study, we observe that smaller (nano-scale) particles tend to achieve lower peak temperatures than the larger particles. While the small size of these particles allows them to heat up quickly, it also results in them cooling more quickly after exiting the hottest parts of the gaseous flame. The smaller particles also have a higher mass percent of inert oxide layer, due to their greater surface area. This added heat sink also likely contributes to the lower observed temperature. The formation of local hot spots in the µm-Al seeded flames leads to an ignition event when the condensed-phase temperatures exceed the melting point of Al_2O_3. No such ignition event was observed for either of the boron containing powders, and the condensed-phase temperatures stayed below the boiling point of B_2O_3. The fast increase in heat flux, however, with additional concentration for the RMNP-seeded flames suggests they have the highest gravimetric energy density of all the materials tested.

2. Experimental

2.1. Fuels

Several commercial powders were purchased for comparison to the sonochemically generated RMNPs. Micrometer-sized aluminum (µm-Al) was procured from Alfa Aesar, which specifies the particles as spherical with an average particle diameter of 3-4.5 µm, and with active metal content of 97.5 % (metals basis). Nanometer-Al (nm-Al) was purchased from SkySpring Nanomaterials, with active metal content of ~80 %, as determined by NaOH titration, as well as poly(methyl methacrylate)-protected bomb calorimetry [14]. Although the manufacturer lists the average particle diameter as 60-80 nm, dynamic light scattering (DLS) measurements and SEM imaging show that the particles are much larger, with an average diameter of approximately 370 nm, and have a broad size distribution. Boron powder (SB95) was purchased from SB Boron Corporation, with active boron content of 95%–97% and particle size range of 0.5–0.8 µm, according to the manufacturer data sheet. Aluminum oxide (Al_2O_3) nanopowder was purchased from Sigma Aldrich, who specified the particles were less than 50 nm in diameter.

The RMNPs were synthesized using a process outlined in detail in previous publications [11,13]. First, in an Ar atmosphere glovebox, $TiCl_4$ was dissolved in a special flask equipped with a large Teflon-valved neck and a sidearem, and charged with Et_2O. Then $LiAlH_4$ (LAH) and $LiBH_4$ (LBH) were separately dissolved in Et_2O in a standard Schlenk flask. Both vessels were placed on a Schlenk line under N_2 purge, and the mixture of LAH and LBH was added to the $TiCl_4$ solution under N_2 atmosphere via cannula while agitated by a benchtop ultrasound bath. The reaction was allowed to proceed for 18 h while agitated by sonication and the byproduct H_2 gas was allowed to vent during reaction. For this work, the stoichiometry defined by Eq. (1) was used.

$$TiCl_4 + LiAlH_4 + 3LiBH_4 \xrightarrow{Et_2O} 4LiCl + TiAlB_3H_y + \left(8 - \frac{y}{2}\right)H_2 \tag{1}$$

The black powder that was produced during the reaction was then dried and washed with Tetrahydrofuran (THF) to remove the LiCl byproduct. The powders were then heat treated under vacuum (10-20 mtorr) at 150°C overnight (16–18 hrs). Up to this point all samples were handled under inert atmosphere. Prior to being used in burner experiments, the powders were transferred to a flow box where they were slowly exposed to air to remove the possibility of a runaway reaction. While these particles have features on the nanoscale, the overall particle dimensions are on the order of micrometers [14]. A cryogenic ball milling process was used to generate finer powders for comparison. In this process, 2 g of Ti:Al:3B material is placed in a 4 mL stainless steel milling cup together with 5 g of 3.5 mm diameter stainless steel milling media. The cup is then placed in the mill, cooled to LN_2 temperature, and milled at 25 Hz for 120 min. After milling, the powders have an average particle size of 380 nm, as determined by DLS measurements [14].

2.2. Aerosolized powder burner

The aerosolized powder burner (APB) designed and used for this study is based on the experiments published by Goroshin et al. [17,19]. A diagram of the burner is pictured in Fig. 1. Premixed methane and air, with an equivalence ratio (Φ) of 0.63 and a total flow rate of 35 l/m, travels through a 40-µm circular slit, creating a high-velocity flow (~250 m/s) that entrains and aerosolizes