Technical Notes

Enhancement of Solid Fuel Combustion in a Hybrid Rocket Motor Using Amorphous Ti–Al–B Nanopowder Additives

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I. Introduction

ADDITION of metallic ingredients is of interest to increase energy density, flame temperature, and regression rate of solid fuel compositions considered for propulsion applications [1–7]. Additives with high specific surface areas can help to achieve fast ignition and short particle burn duration, while promoting high conversion efficiency within the residence time of a combustor. The oxide content, which increases with specific surface area, results in reduced energy density of the composition, for a given additive loading fraction. Introduction of nanoscale additives during fuel processing presents additional difficulties, such as increasing mix viscosity, enhanced or catalyzed curing resulting in reduced processing time, and particle aggregation. During combustion, particle sintering and/or melt coalescing can form large agglomerates that require increased burn duration, which may result in expulsion of unreacted mass, reduced conversion efficiencies, and multiphase flow losses through the nozzle of the propulsive device. Furthermore, because of slow regression rates of solid fuels, the gas flux from the surface is often too low to overcome surface tension and entrain particles, even of nanometer size.

To address the above-mentioned issues, researchers have been investigating innovative methods for nanoparticle addition to fuels and energetic materials, with emphasis on preserving the active content as well as retaining the primary particle size. For example, Zachariah and co-workers have produced micron-sized meso-particles formed by aggregating nanoscale particles coated with an energetic binder [8–10]. These mesoparticles are designed to prevent nanoparticle sintering and to disrupt at or above the solid (liquid)/gas interface and distribute the nanoparticles for individual burning.

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Enhanced reactivity may also be achieved through milling particles with a second reactive material, which promotes a highly mixed structure with a large interfacial surface area [11,12]. In another novel approach, researchers at the Naval Research Laboratory (NRL) have developed a wet sonochemical synthesis of relatively air-stable reactive mixed-metal nanopowders (RMNPs) [13–17]. Metals containing hydrides and chlorides are reacted in a mostly unreactive organic solvent under continuous sonication to produce mixed metal intermetallic reactive powders (Ti–Al–B compositions). Bomb calorimetry analysis has shown that RMNP samples have up to 19% higher volumetric and 24% higher gravimetric energy densities relative to comparable nanometer-sized aluminum (nAl) particles [14].

In the current study, Ti–Al–B RMNPs, which also contain lithium, hydrogen, carbon, and chlorine both from solvent activation and from the original metal hydride precursors, are considered as a potential energetic fuel additive, and are introduced at a 10 wt% loading to hydroxyl-terminated polybutadiene (HTPB) fuel for analysis. Combustion studies were conducted using a static-fired motor to investigate the influence of the RMNPs on the regression rate of HTPB using gaseous oxygen as the oxidizer. As a means of comparison, solid fuel samples containing the same loading of nAl particles were investigated as well.

II. Experimental Setup

A. Grain Manufacturing

Grains were manufactured in batches of two, with formulations targeting 10 wt% of the metallic additive and 2.5 wt% plasticizer. Both as-prepared and ball-milled RMNPs were considered in this study. The particles were stored under argon at elevated pressure. The pressurized container was located within a glove box that was purged for a minimum of 30 min before particle handling. 2-Ethylhexyl acrylate (EHA, $C_{11}H_{20}O_2$, plasticizer), which was found to extend the working time after curative addition, was added directly onto the particles and mixed for 5 min. Polybutadiene resin (R-45M) was then added to the composition and mixed by hand for 15 min, after which the curative (Isonate 143L, MDI) was added and mixed by hand for 5 min. The fuel mixture was then vacuum degassed for 10 min under a reduced pressure of ∼30 torr. Finally, the phenolic cartridges were pour-filled and allowed to cure under ambient conditions for at least 48 h before turning to the required length (14 cm, or 5.5 in.) and porting (6.35 mm, or 0.25 in.). Images depicting a cast, cured, and ported solid fuel grain (containing 10 wt% ball-milled RMNPs) are presented in Fig. 1.

B. Motor Setup

Combustion experiments were conducted using a static-fired rocket motor. A schematic of the chamber and feed system and recorded data obtained from one motor firing are provided in Fig. 2. Gaseous oxidizer and inert gas flows were initiated through electropneumatically actuated valves and metered through choked orifices. A custom LabVIEW control sequencing program was used to sequence valves, initiate the motor firing, and control the firing duration. Pre- and post-chamber liners and nozzles were machined from graphite. The combustion chamber wall and graphite liners are ported to permit igniter insertion, rupture disk/pressure relief, and measurement of pressure during the experiment. The chamber is sled-mounted to facilitate instantaneous thrust measurement when required. Further details are available in the literature [18,19].

III. Results and Discussion

Regression rates of RMNP- and nAl-loaded (10 wt%) HTPB samples were experimentally evaluated over a range of oxidizer mass
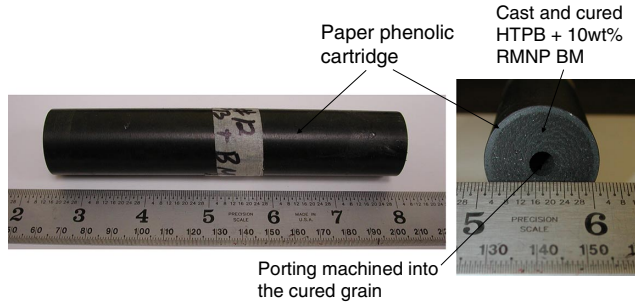
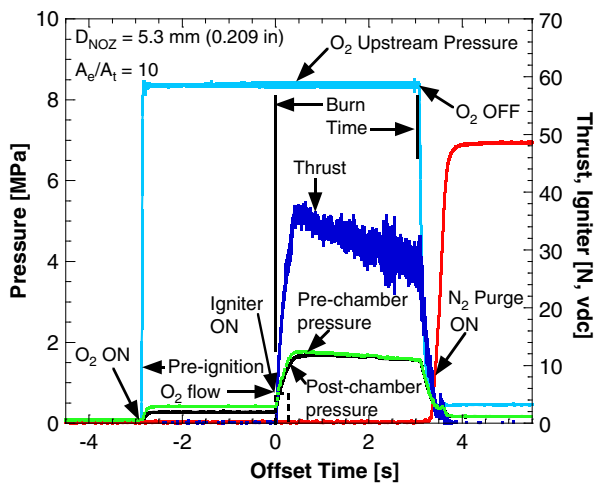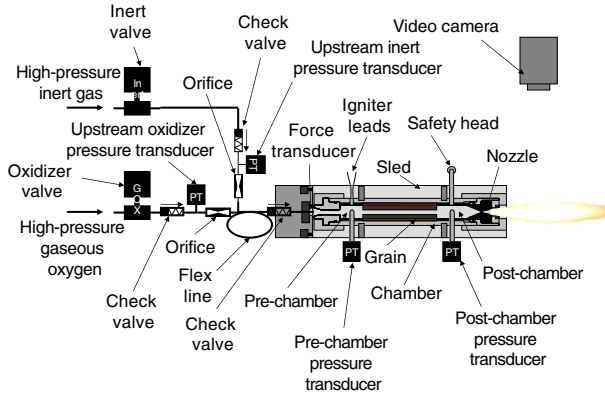**Fig. 1   Cured and ported solid fuel grain (HTPB + 10 wt% ball-milled RMNPs).**

Fig. 2   Hybrid motor schematic (top, modified from [18]) and recorded firing data (bottom).
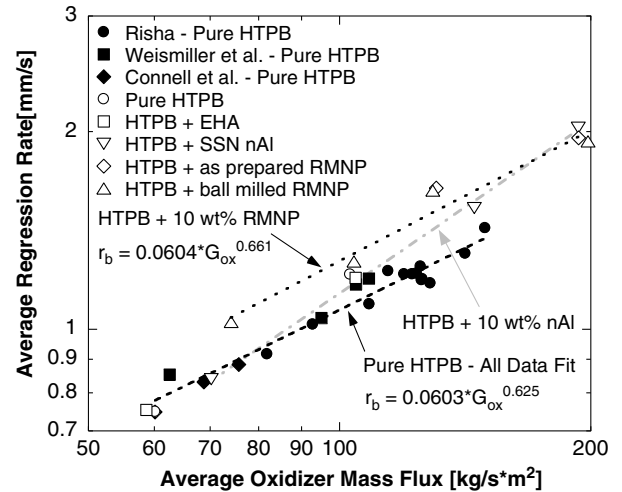

Fig. 3   Average solid fuel regression rate data obtained from solid fuel grain analysis over a range of oxidizer mass flow rates at a nominal motor pressure of 221 ± 8 psia. Shown with pure HTPB regression rate data from [6,19,20].

maximum heat feedback is achieved. Thus, under these conditions, it is postulated that the regression rate slope will reduce and follow a slope similar to the baseline fuel, with an elevated regression rate value achieved for a given oxidizer mass flux, similar to the RMNP-loaded fuel. Theoretically, the RMNP- and nAl-loaded fuels yield similar reaction temperatures; however, where the particles react and release heat will affect the rate of fuel pyrolysis through heat feedback. If the particles react with oxidizing species in the region between the flame zone and molten fuel surface, the rate of pyrolysis may be enhanced. Thus, at low mass flow rates, the nAl does not contribute to the heat release, whereas the entrained RMNP does and therefore continues to enhance the regression rate.

Results from thermogravimetric analysis provided by Epshteyn et al. show that mass loss for this RMNP formulation initiates around 200–300°C, with rapid mass loss occurring near 500°C (773 K) [14]. Fuel surface temperatures (measured during lab-scale motor firings) are significantly higher, ranging from approximately 930 to 1188 K [21]. Thus, gas evolution from heating RMNPs in the near surface region is postulated to aid in particle ejection from the molten fuel surface and may explain the enhancement RMNP addition imparts relative to nAl under lower flow conditions (Fig. 3). Gas evolution may also reduce particle aggregation and sintering as observed with other energetic particle composites [9]. Varied pressure motor results (Fig. 4) show a decrease in regression rate with

flow rates, varying the nozzle throat area to maintain similar motor pressures between experiments. In addition, several experiments were conducted over a range of pressures (using a fixed oxidizer mass flow rate) to evaluate the influence of chamber pressure on regression rate for the RMNP loaded fuel.

Measured average regression rates of RMNP-loaded fuels exhibited a similar slope as the pure HTPB baseline, but were approximately 20% greater, as shown in Fig. 3. The nAl-loaded solid fuel exhibited a steeper burning rate slope, reaching a similar regression rate as the RMNP samples for the highest oxidizer flow rate. Under low oxidizer flow conditions, the Al appears to accumulate within the melt, forming a slag layer within the grain port. As the rate of solid fuel/binder regression increases with oxidizer flow, the fraction of Al entrained by the gaseous pyrolysis products would be expected to increase. Combustion of the entrained Al results in enhanced heat feedback to the surface, which increases the surface temperature gradient, resulting in a higher fuel regression rate. In the limit, Al is entrained at the rate at which the HTPB fuel regresses (i.e., no accumulation within the melt layer) and the
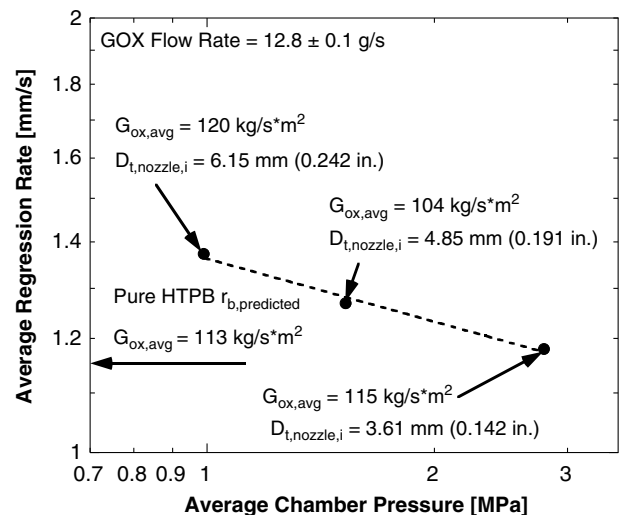

Fig. 4   Measured regression rate for RMNP-loaded HTPB as a function of pressure. The average oxidizer mass flux was 113 ± 7 kg/(s · m²).

increasing chamber pressure, whereas experiments conducted using pure HTPB have exhibited a relative independence of regression rate on pressure (which is expected due to the diffusion-controlled combustion process) [6]. With increasing pressure, the velocity of gases evolving from the heating of RMNP material decreases, leading to reduced particle ejection and subsequently influencing the rate of pyrolysis through the heat feedback mechanism, resulting in a lower measured regression rate.

Finally, performance calculations were performed using the Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications (CEA) [22] by estimating heats of formation for the RMNP materials from previously measured elemental composition and heats of combustion [14]. When 10 wt% of the RMNPs was added to HTPB fuel and reacted with LOx over a range of O/F ratios (1.5–4), the results suggested an improved specific impulse of about 1–2 s over an equal addition of nanoaluminum to the HTPB. However, the estimated heats of formation have considerable uncertainty due to difficulty in obtaining accurate measurements of the RMNP elemental composition. In addition, replacing nAl with RMNPs was found to reduce the fraction of condensed-phase product species by approximately a factor of 3. Condensed phase products can accumulate within the combustor and/or result in multiphase flow losses during acceleration within the expansion region of the nozzle. The absence of an oxide coating on the RMNPs is beneficial to these results, particularly when compared with the nanoaluminum used in the present study where the presence of the oxide reduced the active aluminum content to 80%. Furthermore, having the boron bound within the intermetallic mixed-metal matrix mitigates the presence of B_2O_3 and should therefore ameliorate long ignition delay times typically associated with use of boron particles. Removal of B_2O_3 from the particle surface [23] and substitution of metal-boride compounds [24] have exhibited reduced particle ignition delays. Although these results are encouraging, further research is required to obtain more accurate heats of formation.

IV. Conclusions

Combustion of solid fuels containing nAl and Ti–Al–B reactive mixed-metal particles (RMNPs) was experimentally investigated using a static-fired cylindrical motor. Addition of 10 wt% RMNPs to HTPB solid fuel increased the measured regression rate by approximately 20% for all oxidizer mass flow rates considered. The slope of the burning rate curve mimics that of pure HTPB. Regression rates measured for HTPB containing 10 wt% nAl exhibited an increased slope, ranging from values comparable to pure HTPB under low-flow conditions and reaching the RMNP-loaded regression rate at the highest flow rate. Postfiring observations suggest that under reduced-flow conditions, an increasing fraction of nAl accumulates in the melt layer. Evolution of gaseous species from heating RMNPs may aid in particle ejection and reduction of particle aggregation and sintering. Entrainment and subsequent combustion of the RMNPs contributes to the overall heat release, enhancing the regression rate relative to the nAl-loaded fuel under reduced oxidizer flow conditions

Acknowledgments

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