Experimental Evaluation of Plain Metal Additives for Solid-Fuel Propulsion Applications

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1 Introduction

Hybrid rocket engines (HREs) have unique advantages in comparison to pure solid or liquid propellants, but several drawbacks have hindered their widespread adoption. The most cited drawback, characteristically slow solid fuel regression, has led to the development of several enhancement strategies including entrainment-type fuels, energetic additives, and augmented combustion port geometries. Inclusion of energetic additives can increase fuel regression as well as improve performance (specific impulse or density specific impulse). Most research efforts into energetic additives for application in HREs and solid fuel ramjets (SFRJs) have included various forms of carbon, metals, and metal hydrides, where the majority of this work has focused on aluminum particles. Detailed reviews of these topics are provided elsewhere by the authors [1] or by Risha et al. [2]. Key historical studies are summarized, as follows. Inclusion of energetic additives for performance enhancement of HREs and SFRJs is a widely researched topic, but the fundamental phenomena and factors governing the observed behaviors are not well characterized. Potential regression rate enhancement stems from increased flame temperatures, enhanced radiative heat transfer to the fuel surface, and heat release due to additive exothermic reactions near the surface. However, accumulation of partially or unreacted additive particles on the fuel surface can negatively impact performance by blocking heat transfer. Some of these difficulties arise from inefficient ignition and combustion of the additive particle. In general, emphasis has been placed on research involving aluminum and boron at both the micro- and nano-scale.

The current study aimed to evaluate alternative, potential metallic additives for use in HREs and SFRJs alongside standard aluminum and boron particles. This objective was completed through an in-depth theoretical performance analysis focused on HRE applications followed by a series of ballistic experiments completed on a lab-scale HRE, as presented in the rest of this paper. Further details on the study presented herein are available elsewhere. [1]

2 Theoretical Performance Analysis

The inclusion of energetic additives in HRE and SFRJ fuels can improve their gravimetric or volumetric oxidation, which can also translate to improved specific impulse or density specific impulse, respectively. The potential of these additives for performance enhancement in HREs was evaluated through a series of chemical equilibrium analysis (CEA) computations completed with Praqsys's Cequel program. Fuel

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formulations encompassing plain HTPB and HTPB loaded with 50% (by mass) of each additive were reacted with liquid oxygen (LOX) or nitrous oxide (N_2O) at a combustion pressure of 1,000 psi (6.89 MPa). Propellant performance and combustion gas properties for these fuel formulations are plotted against oxidizer-to-fuel (O/F) ratio for fuel reacting with LOX in Fig. 1. The computed parameters include adiabatic flame temperature, characteristic velocity, specific impulse, and density specific impulse. The density specific impulse as defined herein is normalized by specific gravity: $I_{sp,v} = (\rho/\rho_{H_2O})I_{sp}$. Increases in the maximum adiabatic flame temperature are noted for approximately half the additives, where Be, Al, B, Ti, Zr, and Mg, produce the largest increases, respectively, regardless of oxidizer. For both oxidizers, even though some of the additives (Be and B) have higher gravimetric heats of combustion, the theoretical specific impulse is not improved by the inclusion of any of the evaluated additives. However, the inclusion of most additives yields increases in the density specific impulse, which is more relevant for volume-limited propulsion applications and can also improve a rocket system's ΔV. In addition, the O/F ratio where optimum performance is noted shifts to lower values, so that less oxidizer is required to achieve this performance. This O/F shift is desirable for HRE applications in which all oxidizer is stored in the rocket prior to launch but may be undesirable for some SFRJ applications where oxidizer is captured from the local atmosphere. The highest optimum density specific impulse for fuels reacting with LOX are Zr, W, Zn, Ti, B, and Sn, respectively; and for fuels reacting with N_2O are B, W, Zr, C, Ti, and Zn, respectively. It is worth noting that two-phase flow losses were neglected in the ideal calculations presented herein, which can be appreciable for fuel formulations with high concentrations of some metal additives.

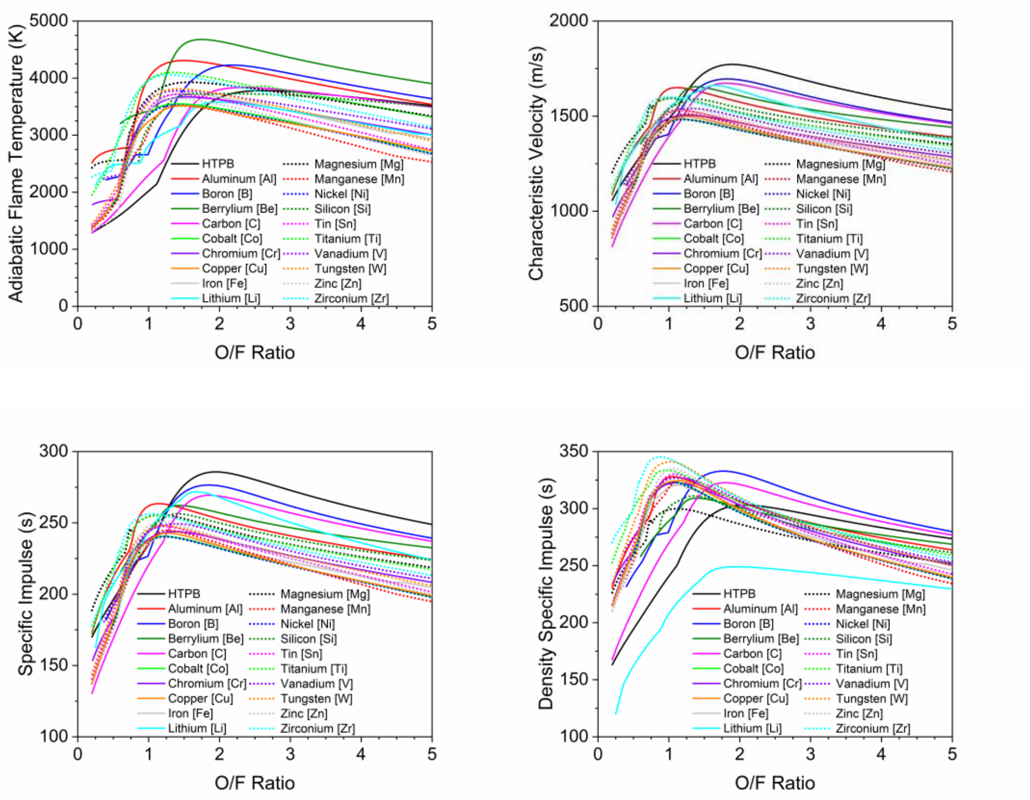

Figure 1: Theoretical performance of HTPB fuel loaded with selected metals at a mass concentration of 50% burning in liquid oxygen (LOX) at a pressure of 1,000 psia (6.89 MPa). Plots depict (top left) adiabatic flame temperature, (top right) characteristic velocity, (bottom left) ideal specific impulse, and (bottom right) ideal density specific impulse.

3 Experimental Methods

The objective of the present project was to evaluate potential performance enhancement and combustion behavior associated with the inclusion of candidate metal particles. In addition to standard additives (micro-Al, nano-Al, and nano-B), several additives were chosen (micro-Ti, micro-Mg, micro-Zr, and Mg-coated nano-B) based upon the previously presented theoretical performance calculations, pricing, and availability. All additive particles were characterized by scanning electron microscopy (SEM) or transmission electron microscopy (TEM) imagining techniques. Key attributes of the additives are provided in Table 1 and an example TEM analysis is shown in Fig. 2 for the Mg-coated nano-B particles.

Table 1: Key attributes of the metallic additives evaluated herein as provided by the manufacturer(s).

Additive	Manufacturer	ID	Size (μm)	Purity (%)	Geometry
micro-Al	Valimet, Inc.	H-30	20-30	99.7	Spherical
micro-Ti	US Research Nanomaterials, Inc.	US-1038M	45	99	Irregular
micro-Mg	US Research Nanomaterials, Inc.	US-1060	40	99.9	Flake
micro-Zr	US Research Nanomaterials, Inc.	US-1040M	75	99	Irregular
nano-Al	US Research Nanomaterials, Inc.	US-1043	0.1	99.9	Spherical
nano-B	SB Boron Corporation	SB-95	0.7	92.1-96.0	Irregular
nano-MgB	Mach I Specialty Chemicals, Inc.	-	0.7	88	Irregular

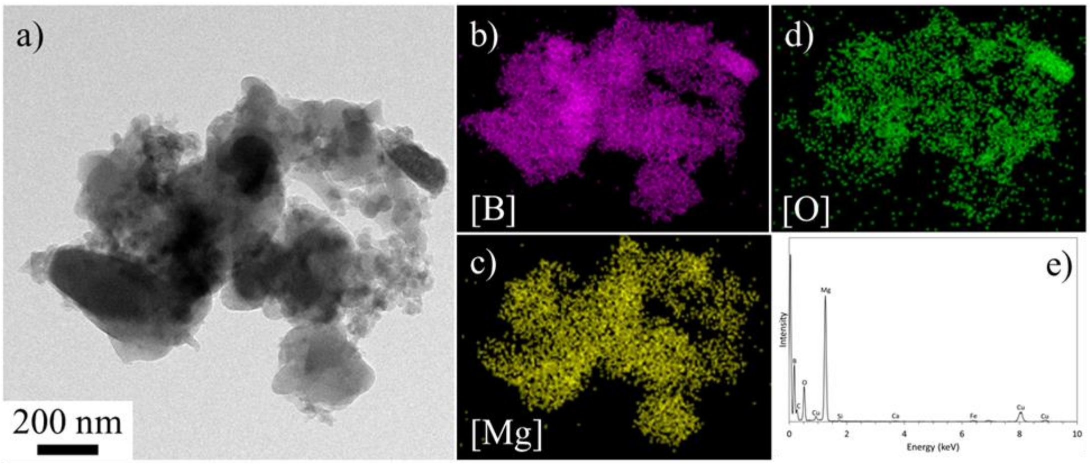

Figure 2: TEM imaging of a magnesium-coated boron nanoparticle agglomerate at a magnification of 15 kX. a) raw TEM image; elemental EDS maps of b) boron, c) magnesium, and d) oxygen; and e) EDS spectrum.

Plain HTPB and metal-loaded formulations (10-30% by mass) were manufactured and burned in gaseous oxygen (GOX) crossflow. An experimental schematic of the HRE is shown in the left image of Fig. 3. Oxidizer flow is controlled with a mass flow controller, ignition of fuel grains (ID = 2 mm, L = 5 cm) is initiated by a solid propellant squib, and combustion is terminated by terminating oxidizer flow. A representative set of transient data is shown in the right plot of Fig. 3. Further details on the design and operation of the HRE experiment are provided elsewhere by the authors [1]. The final combustion port diameter is computed by the mass-loss method ($D_f = \{[4(m_i - m_f)/\pi\rho_f L] + D_i^2\}^{1/2}$). Key ballistic parameters reported herein include the average regression rate ($\bar{\dot{r}} = (D_f - D_i)/2t_b$), average oxidizer mass flux ($\bar{G}_{ox} = 16\bar{\dot{m}}_{ox}/\pi(D_i + D_f)^2$), characteristic velocity ($\bar{c}^* = \bar{P}_c A_t/(\bar{\dot{m}}_{ox} + \bar{\dot{m}}_f)$), combustion efficiency ($n_{c^*} = \bar{c}^*/c^*_{th}$), and residence time ($t_r = V_c\rho_c/\dot{m}_T$).

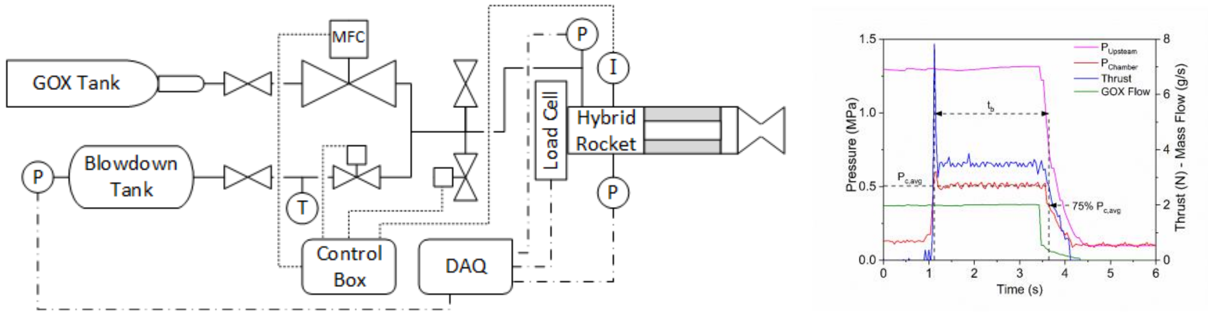

Figure 3: (left) Schematic representation of the hybrid rocket ballistic experiment. (right) Representative transient data traces for plain HTPB burning in GOX at a chamber pressure of approximately 0.52 MPa (75 psia).

4 Results and Discussion

Plain HTPB and HTPB loaded with 10%, 20%, and 30% of each additive were burned in GOX at pressures ranging from 0.5-0.7 MPa (75-100 psia). The results for plain HTPB and fuels loaded with micro-Al and micro-Zr are presented herein, and ballistic data for other fuel formulations are discussed elsewhere by the authors [1]. The regression rates and combustion efficiencies for relevant fuel formulations are shown in Fig. 4. The baseline plain HTPB regression rate data agree well with similar data presented in the literature in terms of quantitative value and the observed oxidizer mass flux exponent (~0.61). In general, the inclusion of micro-Al in the solid fuel reduced the observed regression rate. This trend is more observable at higher oxidizer mass fluxes and higher additive loadings. This finding is in direct conflict with most of the data available in the literature which indicate the inclusion of micro-Al yields regression rate enhancement in solid fuel combustion. However, disparate findings which agree with the current study's findings can also be found in the literature.

The reaction time of aluminum particles has been shown to be dependent on pressure [3-4], and the regression rate of fuels loaded with aluminum has also exhibited pressure-dependent behavior [5-6], both of which could play a significant role in the observed trends. More explicitly, the data collected herein were for motor firings at approximately 75-100 psia (0.5-0.7 MPa), which is generally lower than previous investigations where regression rate enhancement due to aluminum inclusion was observed. In general, these regression rate enhancements are generally attributed to enhanced radiation heat fluxes and energy release from metal oxidation near the surface of the fuel. [2] However, if the micro-Al additive is not reacting rapidly enough due to the lower-pressure environment, oxidation and combustion may not take place in the combustion port fuel grain or near the fuel surface, and instead in the post-combustion chamber.

Strand et al. [5-7] observed that micro-aluminum additives included in HTPB burning in GOX would agglomerate on the fuel surface and periodically detach from the surface. Similar findings are reported throughout the literature for fuels loaded with various micro- and nano-additives. Post-combustion analysis of combustion ports and fuel surfaces revealed that for fuels loaded with micro-Al, the presence of the surface-layer increases with additive concentration. This accumulated surface layer acts as a thermal isolator and hinders heat transfer from the diffusion flame to the solid fuel, which is termed the blowing effect. Increased loading of micro-Al led to further decreases in the observed regression rate. This trend is likely due to accumulation of more agglomerations and additive mass on the fuel surface which further decreases the heat flux that reaches the virgin fuel.

At moderate oxidizer mass fluxes, mass diffusion processes dominate the fuel regression rate behavior, but at lower oxidizer mass fluxes, thermal radiation processes dominate the regression behavior [6]. The reduced regression rates accompanied by micro-aluminum addition are more observable at higher oxidizer mass fluxes which results in a decreased oxidizer mass flux exponent (n). This observation may indicate that there is some combustion of the aluminum in the combustion port yielding enhanced radiation heat transfer.

The fuel formulation with 10% micro-Zr outperformed the baseline HTPB fuel in terms of fuel regression and mass loss rate, while further loading of micro-Zr yielded decreased regression rates. Furthermore, the 10% micro-Zr fuel formulation exhibited the highest regression rates of all fuels evaluated herein. Once again, the observed trends were generally more prevalent at higher oxidizer mass fluxes The reduction in regression rate accompanying the inclusion of most of the additives is attributed to a combination of slow metal reactions which may take place in the post-combustion chamber, rather than the combustion port, and heat transfer-blocking effects derived from accumulation of mass on the fuel surface layer. The enhanced regression rate and increase in the oxidizer mass flux exponent accompanied by the addition of 10% micro-zirconium led to the deduction that the blocking effect is the more dominant phenomenon of the two.

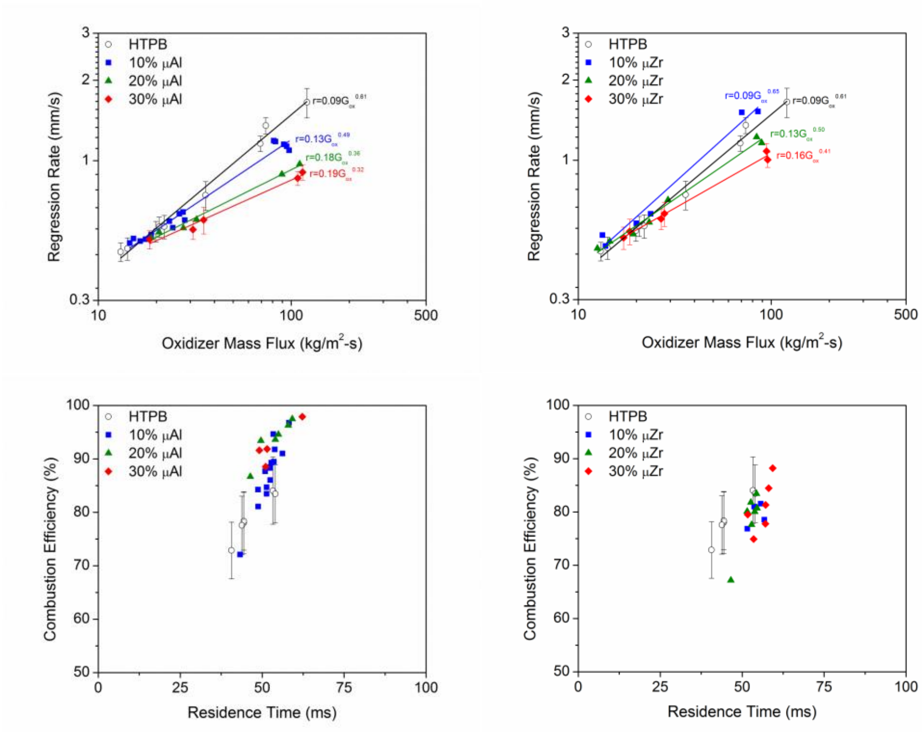

Figure 4: (Top) Regression rates and (bottom) combustion efficiencies for plain HTPB and HTPB loaded with (left) micro-Al and (right) micro-Zr burning in GOX.

Measured combustion efficiencies of solid fuel ballistic experiments are generally plotted against the average O/F ratio within the literature, presumably since higher oxidizer concentrations are expected to yield more complete combustion. However, these types of plots yielded no general trends in the current investigation. Alternatively, the measured combustion efficiencies of all motor firings are plotted against the residence time in the combustion chamber. In general, the combustion efficiency of all motor firings increases with increasing residence time, as expected. Furthermore, the combustion efficiencies of the baseline and the micro-aluminized motors collapse onto a single trend which approaches a combustion efficiency of 100% near a residence time of 75 ms. The micro-Zr fuel formulations exhibit similar combustion efficiency which are slightly lower than the baseline fuel at similar conditions. These observations suggest that although chemistry (e.g., O/F ratio and additive type) probably does play a role in determining the combustion efficiency of solid fuel combustion, the residence time may be the more dominant factor. Furthermore, given the basic design of the current ballistic stand, the current results also suggest that high combustion efficiencies can be achieved without post-combustion mixing devices if sufficient post-combustion chamber volume were included in system designs.

4 Conclusion

Hybrid rocket performance can be augmented by the inclusion of energetic additives, such as metal fuels. In comparison to plain HTPB, a historical HRE and SFRJ fuel, the theoretical gravimetric and volumetric heat of combustion of several metals are greater. Detailed CEA calculations were carried out for HTPB fuels loaded with various metal additives reacting with LOX and N_2O. These computations demonstrated the potential for metallic additives to yield significant improvement of solid fuel systems, especially in terms of density specific impulse.

The regression rates and combustion efficiencies of plain HTPB and HTPB loaded with several metal additives at various loadings burning in GOX were evaluated on a lab-scale HRE. In general, the inclusion of any of the selected additives led to a reduction in the regression rate and minor changes in the combustion efficiency behavior, except for the micro-Zr additive which yielded increases in regression rate and fuel mass flux. These observed trends were more prevalent at higher oxidizer mass fluxes and were attributed to heat transfer blocking effects derived from a fuel-surface accumulation layer. Combustion efficiency data of the plain HTPB and metal-loaded fuel formulations were not well correlated with the average O/F ratio, but they were well correlated to the residence time. High combustion efficiencies (>95%) were achievable for all fuel formulations when a satisfactory residence time (<100 ms) was realized. Zirconium appears to be the best metallic additive available since it can yield the highest specific density specific impulse at the lowest O/F ratio without resulting in decreased performance.

Disparate results in the literature and observations gathered herein indicate the underlying physical mechanisms governing particulate additive migration, aggregation/agglomeration on the fuel surface, entrainment into the oxidizer crossflow, and accompanying ignition/combustion processes are not well understood. Future research efforts aimed at evaluating these simultaneous phenomena would greatly benefit the community and our understanding of how to positively augment HRE and SFRJ combustion processes. In particular, a lab-scale slab burner with optical capabilities that spanned a wide range of operating conditions (e.g., port diameter, oxidizer mass flowrate, and chamber pressure) could prove useful in gaining a better understanding of the surface accumulation layer and factors that govern additive behavior therein. In addition, future studies involving Zr-based additives should be conducted to evaluate its true potential for HRE and SFRJ applications.

References

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