Investigation of Micro- and Nano-Catalytic Additive Effects on Ammonium Perchlorate Combustion

Felix A. Rodriguez, James C. Thomas, Thomas E. Sammet, David S. Teitge,
and Eric L. Petersen
J. Mike Walker '66 Department of Mechanical Engineering, Texas A&M University
College Station, Texas, USA

1 Introduction

AP is used extensively as the oxidizer component of composite propellants and plays a significant role in the overall performance. Gaining a deeper understanding of the effects metal oxide catalysts have on the burning rates of AP alone can allow for better control over composite propellants. The purpose of this investigation was to characterize the burning rates of AP pellets with micro- and nano-sized metal oxide catalytic additives. This characterization was done by performing microscopy analyses and ballistic testing on AP pellets with titanium oxide (TiO_2) and iron oxide (Fe_2O_3) in both micro- and nano-sized forms.

Several studies have incorporated nano- and micro-additives to quantify their effect on composite propellants [1-4]. Kshirsagar et al. [1] reported a 2% increase in burning rate from the micro- to the nano-manganese dioxide (MnO_2) composite propellants. Reid et al. [2] studied several types of nano-scale TiO_2 into AP/HTPB composite propellants. The maximum increase in burning rate was reported to be 30% relative to the baseline formulation. Marothiya et al. [3] incorporated AP with micro- and nano-Fe_2O_3 embedded on the surface in aluminized composite propellants and reported an increased burning rate of 27.4% and 7.3%, respectively. Stephens et al. [4] investigated the effects of micro- and nano-aluminum on AP/HTPB composite propellants and arrived at the conclusion that AP concentration and size affect whether nano-aluminum causes an increase in burning rate. It can be extrapolated from the literature that the positive effects of nano-scale particles over their micro-scale counterparts are situationally dependent.

Additional investigations of the effect Fe_2O_3 has on reagent and plain AP alone have been conducted previously. Friedman et al. [5] investigated the deflagration rate of AP pellets pressed from reagent-grade AP of varying particle sizes and preparation methods. Testing of the 'as-received' AP resulted in upper and lower deflagration limits (UPDL and LPDL) of 4.55 (660 psi) and 30.34 MPa (4,400 psi), respectively. Micro-Fe_2O_3 at a mass loading of 3% was found to decrease burning rates at lower pressures and increase burning rates at higher pressures. Boggs et al. [6] studied the combustion of single-crystal AP and pellets pressed from 99.9% pure AP. Additive formulations were manufactured with micro-Fe_2O_3 at 2% and 8% concentrations by mass, and the 2% micro-Fe_2O_3 pellets yielded an increase in the deflagration rate and temperature sensitivity of pure AP. The 8% concentration decreased the burning rate and altered the LPDL to a higher pressure than plain AP. Ishitha et al. [7] investigated

Correspondence to: FRod1214@tamu.edu

the role of Fe_2O_3 through testing of AP pellets, laminate propellants (i.e., sandwiches), and solid propellant strands. This study concluded that 1% Fe_2O_3 pellets had higher burning rates that 1% copper chromate pellets, over the investigated pressure range (500-1000 psi). Marothiya et al. [8] conducted strand burner experiments with AP pellets comparing the effects of mechanically mixed and embedded catalysts. Micro-Fe_2O_3 loading percentages were varied from 0.75-5%. The burning rate of the 1% catalyst loading resulted in the highest burning rate, which was reported to agree with the literature. Multiple suppliers were used for the embedded catalyst samples and, even at the same concentrations, different burning rates were observed. This observation alludes to the importance of additive characterization. Ingole et al. [9] characterized AP pellets with 1% Fe_2O_3 at 303 and 343 K (30 and 70 °C) over a pressure range of 2 to 30 MPa (290-4,350 psi) in a standard Crawford bomb. The burning rates, collected at pressures lower than the LPDL reported in previous studies, and temperature sensitivities were higher than the data collected from earlier studies.

In the current study, TiO_2 and Fe_2O_3 were implemented at various particle sizes (micro and nano) and loadings (0-3% by mass) in AP pellets to investigate their potential catalytic effects on plain AP. A description of the experimental methods will follow along with microscopy imaging, conducted on all relevant additives and representative samples, ballistics testing, discussion of the results, and conclusions.

3 Experimental Methods

The AP utilized herein was high-purity (> 99.9%) and donated by American Pacific (AMPAC) with an average particle size of approximately 250 μm. Previous studies completed by Seetharamacharyulu et al. [27] concluded that the burning rate of AP pellets is independent of the particle size of the AP particles used once the actual density of the AP pellets exceeds 98% of the TMD. The threshold of 98% TMD can be reached by varying the pressing parameters, such as compaction force and dwell time. The average %TMD for all pellets investigated was above about 98%, and this exceeds the threshold previously mentioned.

All formulations were mixed in a Resodyn Resonant Acoustic Mixer (RAM). Mixing parameters implemented in the current study were 2-minute mixing time, 70 g's of acceleration, and 75-85% fill in a 36-mL plastic vial [11]. Pellets were compacted in a custom pellet punch assembly loaded into a Carver M-NE3890 hydraulic press at a force of 5,443 kg_f (12,000 lb_f) for one hour. Samples were sanded on both ends and an inhibitor (Krylon spray paint) was applied to all but one face. Approximately 0.15 g of igniter material (boron potassium nitrate, $BKNO_3$) was weighed and spread out in an even coat over the uninhibited face of the pellet. The sample is placed atop a custom holder with an ignition feed-through; a nichrome wire is placed within the $BKNO_3$ powder and secured to the feed-through; and the ignition system is secured with tape.

The ballistic testing was conducted in a constant-volume strand burner which has the capability of testing up to 55.16 MPa (8,000 psi); for the experiments conducted herein, formulations were tested from 3.45-34.5 MPa (500-5,000 psi). The strand burner has four optical ports that can be utilized to perform various diagnostics and alter the ignition methods. The three optical ports located on the sides of the strand burner allow for mass spectroscopy, high-speed video, and photoreceiver light emission. Ten samples were burned for all formulations, and several formulations were retested to ensure repeatability.

4 Microscopy Characterization

Scanning electron microscopy (SEM) images of the micro-additives were taken on a Tescan VEGA3 SEM to evaluate fundamental particle sizes. Representative images of the micro-TiO_2 and Fe_2O_3 particles are shown in Fig. 1.

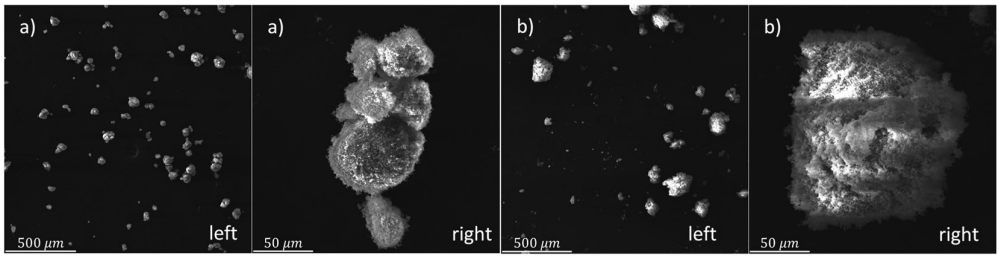

Figure 1 SEM images of a) micro-TiO_2 particles b) micro-Fe_2O_3 particles. (left) Several particles at a magnification of 100X and (right) a single particle at a magnification of 850X.

Transmission electron microscopy (TEM) images of the nano-additives were taken on a JEOL 1200 EX TEM to evaluate their fundamental particle sizes. The TEM images indicate fundamental particle sizes which are in good agreement with the manufacturer-provided specifications.

SEM images of representative AP pellets containing micro- and nano-additives were taken on a Tescan VEGA3 SEM to evaluate the dispersion and homogeneity of these additive within the system. Representative SEM images of AP pellets containing 1% micro-TiO_2 are shown in Fig. 2. Similar images were taken of a 1% micro-Fe_2O_3 pellet. In general, the micro-additives are well-dispersed throughout the pellet and are not significantly agglomerated. Furthermore, the BSE and EDS images show good agreement in terms of additive particle location, demonstrating the utility of either method for future characterization purposes.

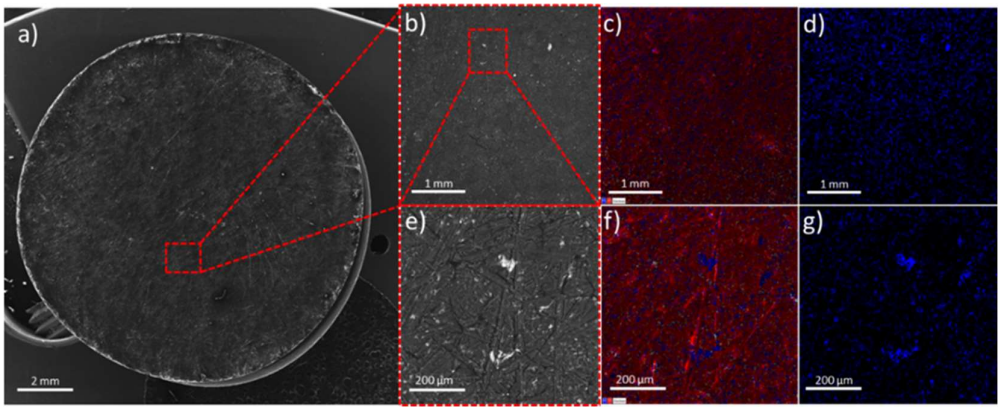

Figure 2 SEM imaging of an AP pellet containing 1% micro-TiO_2. a) Plain, wide-view SEM image of the entire pellet at a magnification of 15X. b-d) 50X magnification views of the pellet surface; b) back-scatter image; c) EDS overlay with (red) chlorine and (blue) titanium; and d) EDS overlay of only titanium. The images in e-g) are 250X magnification views of the pellet surface: e) back-scatter image; f) EDS overlay with (red) chlorine and (blue) titanium; and g) EDS overlay of only titanium.

Representative BSE images of AP pellets containing 1% nano-TiO_2 are shown in Fig. 3. Similar BSE images were taken for a 1% nano-Fe_2O_3 pellet. These images suggest that the nano-particles are well dispersed throughout the AP pellet and are not significantly agglomerated.

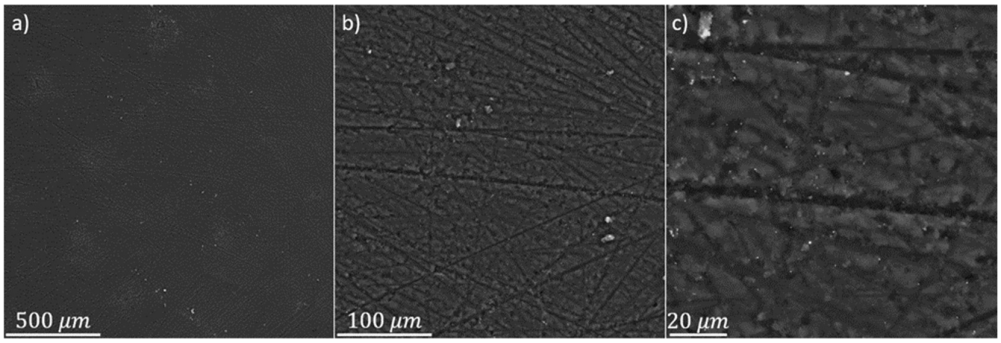

Figure 3 Back-scatter SEM images of an AP pellet containing 1% $nTiO_2$ at magnifications of a) 100X, b) 500X, and c) 1.5kX.

5 Results and Discussion

A facility-specific baseline was developed prior to ballistic testing of AP pellets with catalytic additives. Pellet size and pressing parameters (duration and force) were investigated by Petersen et al. [12]. The parameters implemented herein provided high sample densities (>98%) and repeatable ballistic data.

All the burning rate data collected herein for AP formulations containing micro-TiO_2, micro-Fe_2O_3, nano-TiO_2, and nano-Fe_2O_3 are shown in Fig. 4, along with the corresponding plain AP baseline and trendlines drawn to highlight key trends. To reiterate, the concentrations range from 0.5-3% and 0.25-1% for micro- and nano-formulations, respectively. Open symbols and dashed trendlines correspond to formulations containing micro-catalysts, while closed symbols and the solid black trendlines correspond to formulations containing nano-catalysts.

In general, the formulations containing micro-TiO_2 yielded a reduction in the burning rates at lower pressures (< 13.79 MPa), but were effective at increasing the burning rate at higher pressures. Furthermore, the formulation containing the least amount of catalyst (1%) exhibited the highest burning rates among the formulations containing micro-TiO_2. The formulations containing micro-Fe_2O_3 yielded an increase in burning rate across all pressures evaluated herein and were more effective at higher pressures. Similar to the trends observed for formulations containing micro-TiO_2, the performance of the propellant decreased as the catalyst loading was incrementally increased from 1% to 3%.

Catalytic effects of the nano-TiO_2 and nano-Fe_2O_3 formulations were seen at pressures greater at 11.72 MPa (1,700 psi) and 8.27 MPa (1,200 psi), respectively, in the region of depressed burning rates of plain AP—a well-established literature result. Furthermore, the formulations containing nano-Fe_2O_3 yielded a higher increase in burning rate relative to the nano-TiO_2 formulations. The same decrease in burning rate with an increase in micro-catalyst concentration did not carry over when the nano-forms of the catalysts were implemented, at least within the range of concentrations evaluated herein.

The addition of nano-TiO_2 decreased the burning rates at lower pressures relative to the baseline and all micro-TiO_2 formulations, but displayed better burning rates than the 2 and 3% micro-TiO_2 formulations at higher pressures (>17.2 MPa). The nano-Fe_2O_3 formulations exhibited a similar trend as the nano-TiO_2 formulations. More explicitly, the burning rates were lower than all the micro-Fe_2O_3 formulations at lower pressures, and the effects of the catalyst increased the burning rates towards the burning rates seen by the 0.5 and 1% micro-Fe_2O_3 formulations at higher pressures.

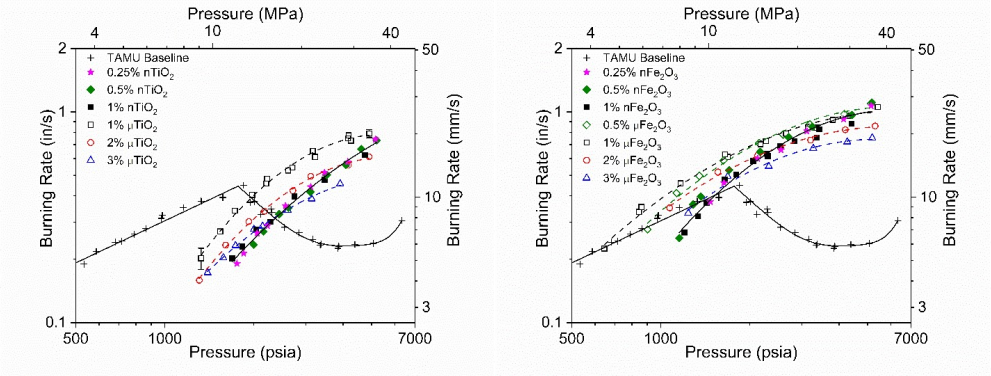

Figure 4: (left) Comparison of burning rate data for micro-TiO_2 formulations with the nano-TiO_2 data. (right) Comparison of burning rate data for micro-Fe_2O_3 formulations with the nano-Fe_2O_3 data.

6 Conclusion

Catalytic micro-additives were successfully incorporated into plain AP and manufactured into pellets. All pellets (0.5" × 0.5") were tested over a pressure range of 3.45-34.5 MPa (500-5,000 psi). Micro-Fe_2O_3 was incorporated at 0.5-3% mass concentrations, while micro-TiO_2 was incorporated at 1-3% mass concentrations. Thorough characterization of all additives and pellets containing these additives was completed using SEM, TEM, and EDS methods. The 1% mass loading of both micro-catalysts showed the highest burning rate with respect to like-additive formulations. The 1% micro-Fe_2O_3 formulation showed the highest global burning rate enhancement across all formulations.

Catalytic nano-additives (nano-Fe_2O_3 and nano-TiO_2) were successfully incorporated into plain AP and manufactured into pellets with mass loadings of 0.25-1%. The change in mass concentration within the evaluated range did not yield a measurable change in burning rate for either additive. The nano-Fe_2O_3 formulation exhibited higher burning rates relative to the nano-TiO_2 formulations. All nano-additives were ineffective catalysts at lower pressures, but did increase the burning rate at higher pressures.

The authors recommend that all future studies make an effort to fully characterize both the additives incorporated in samples and the samples with additives included. Full characterization of the additives implemented in such studies would allow for a more complete understanding of what factors influence the reported results.

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