47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit
31 July - 03 August 2011, San Diego, California

AIAA 2011-5865

Intermetallic Compounds as Fuels for Composite Rocket Propellants

David A. Reese*, Lori J. Groven†, and Steven F. Son‡
Purdue University, West Lafayette, IN, 47907, USA

Alexander S. Mukasyan§
University of Notre Dame, Notre Dame, IN, 46556, USA

Aluminized composite propellants have long suffered from efficiency and thermal challenges related to production of condensed phase slag droplets during operation. In an effort to mitigate the production of large droplets, a mechanically activated intermetallic forming nickel-aluminum compound was substituted for a portion of a propellant's aluminum fuel. The resulting agglomerate size and burning rate of this propellant was compared to a standard aluminized AP/HTPB propellant. Addition of mechanically activated fuel particles increased the burning rate exponent of the propellant, while simultaneously decreasing condensed phase agglomerate size from 235 μm (for the control propellant) to 90 μm (for the propellant containing 75 wt.% Ni-Al fuel). As such, intermetallic forming fuels may provide a route for increasing efficiency in solid rocket motors by simultaneously reducing the need for burning rate catalysts and minimizing two-phase nozzle flow losses.

I. Introduction

Current state-of-the-art solid propellant technology relies on the addition of metallic fuels to increase performance.[1] Micrometric aluminum, the most popular of these additives, tends to form large agglomerates during its combustion process.[2,3] These agglomerate formations severely impact motor performance, as losses appear from velocity and thermal lags in the exhaust stream.[4] Liquid agglomerate droplets may also negatively impact the motor structure, as the collection of these extremely hot particles on internal surfaces, like nozzle entrance cones, may cause thermal failure of these parts. Additionally, the combustion of aluminum particles tends to occur on length scales significantly greater than the size of the near-surface combustion zone formed by the oxidizer-binder system, decreasing burning rate and combustion efficiency.

As a result of these drawbacks, much effort has been spent on the reduction of aluminum agglomerate droplet size in rocket motors. One common method under investigation is the addition of nanometric fuel particles to the propellant mixture. Due to their extremely small size, these nanoaluminum particles burn in a kinetic-limited regime, rather than a diffusion-limited one, resulting in particle ignition and combustion times so short that the traditional "sinter-melt-combust" process of aluminum combustion does not have time to occur. Propellants metalized with nanoaluminum have been observed to have burning rates over 100% greater than propellants based on micron-size aluminum, producing drastically smaller agglomerate structures in the process.[5,6] However, nanoaluminum has not seen widespread use in propellants due to its high cost, low active material content, and incredibly high specific surface area. This high surface area makes wetting of the particles nearly impossible, thus causing mixes to be unworkably viscous and propellants to be prohibitively brittle.

Thus, it would be ideal to engineer a particle with combustion properties on par with those of nanoaluminum while simultaneously retaining the low surface area and high active content of its micrometric

*Graduate Student, School of Aeronautics and Astronautics, 500 Allison Rd., W. Lafayette, IN 47907, AIAA Student Member. Email: reesed@purdue.edu
†Senior Research Scientist, School of Mechanical Engineering, 500 Allison Rd., W. Lafayette, IN 47907, AIAA Member.
‡Professor, School of Mechanical Engineering, 500 Allison Rd., W. Lafayette, IN 47907, AIAA Member.
§Professor, Dept. Chemical and Biomedical Engineering, University of Notre Dame, Notre Dame, IN, 46556.

counterpart. One means of creating such a nanostructured material is the process of high energy ball milling. This process creates a solid state blend of reactive materials with high contact areas and unoxidized interphase boundaries, essentially "mechanically activating" the material. The result of mechanical activation (MA) is a reactive composite particle with significantly decreased ignition energy and ignition temperature requirements,[7] leading to potentially increased heat feedback and reduced condensed phase product size when compared with the results achieved by standard propellant fuel particles, such as aluminum or magnesium.

This work focused on the use of a mechanically activated Ni/Al material to increase the burning rate of an aluminized propellant while simultaneously decreasing the oxide agglomerate particle size. Propellant samples were burned in open air and in a closed bomb. Though the presence of nickel in the exhaust products would indeed detract from the performance of the propellant, other intermetallic systems (e.g., TiB_2) may minimize this performance loss.

II. Experimental

A. Preparation of Mechanically Activated Fuel

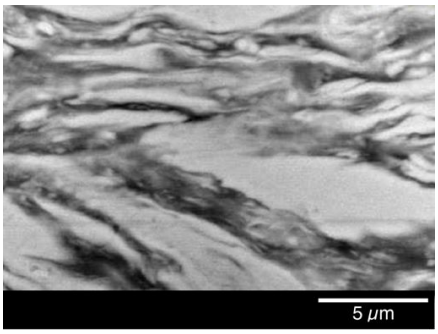


Figure 1: SEM micrograph of mechanically activated Ni-Al material used in this study.[8]

Aluminum powder (3-4.5 μm, Alfa-Aesar) and nickel powder (3-7 μm, Alfa-Aesar) were combined in equiatomic amounts. The mixture was placed into a Retsch PM100 Planetary Mill, along with 300M spherical stainless steel milling media in a 5:1 mass ratio of media to powder. The mixture was milled under argon at 650 revolutions per minute for 15 minutes. The resulting mixture was then solvent ground to reduce its particle size. A pressurized bath of hexanes was used for this procedure to ensure effective heat removal from the particles during the grinding process, preventing cold welding or ignition.

Following grinding, the powder was dried and then passed through a 53 μm sieve to remove any remaining large particles. Finally, the powder was placed into a 25 μm sieve; powder that flowed through was rejected for propellant use, to ensure consistent fuel particle diameters across the control and variable propellant samples. SEM imaging was performed on the finished particles; a typical sample appears in Fig. 1, with regions of aluminum appearing lighter and regions of nickel appearing darker.

B. Preparation of Composite Propellant Samples

Three metalized AP-HTPB composite propellant samples were prepared to determine the effect of mechanically activated (MA) Ni-Al particles on burning rate and agglomerate size. The compositions of each propellant sample are listed in Table 1.

Table 1: Tested propellant formulations with varying amounts of intermetallic material.

	Propellant A	Propellant B	Propellant C
Aluminum, spherical, 25-53 μm	15%	7.5%	3.75%
Milled Nickel + Aluminum, 25-53 μm	0%	7.5%	11.25%
Ammonium Perchlorate, 200 μm	52%	52%	52%
Ammonium Perchlorate, 20 μm	13%	13%	13%
R45M + MDI HTPB Binder System	20%	20%	20%

Propellant A, containing pure aluminum fuel (screened to 25-53 μm, Alfa-Aesar), was designated as the "control" sample, representative of typical composite propellant formulations currently in industrial use. Propellants B and C replaced portions of the metallic fuel component (50 wt.% and 75 wt.%, respectively), with MA Ni-Al. All propellants contained a 4:1 blend of 200 μm and 20 μm ammonium perchlorate (Alliant Techsystems), respectively. Size distributions for these oxidizers are available in references.[9] An 80 wt.%

solids loading was used in all formulations to enable simple processing and minimize the chances of void formation during curing, which would adversely affect burning rate samples. Each propellant was mixed using a Resodyn LabRAM mixer[10] at 60 Gs for 5 minutes; following mixing, the propellant was placed under a partial vacuum to evacuate evolved ammonia and water from the mix. The propellant was cast into 8 mm ID polypropylene sleeves, and cured at room temperature for 48 hours. The resulting strands were removed from the sleeves and sectioned into 25.4 mm lengths for characterization.

C. Burning Rate Determination

Propellant samples were ignited in a quiescent argon environment inside a windowed combustion bomb for burning rate determination. Propellant samples were ignited at five ambient pressures ranging from 20.4 to 81.6 atm. The pressure rise during each burn was noted, and used when computing the burning rate. Reported results are for the mean burning rate at the mean pressure of each data set. Samples were filmed through the polycarbonate window of the combustion bomb at 100 frames per second using a Vision Research Phantom v7.3 high speed camera, and burning rates determined using the GraphClick software package.[11] Pressure and burning rate were plotted on a log-log plot, and a least squares fit applied to determine the parameters in St. Robert's law, which defines burning rate empirically as,

$$r_b = a{P_c}^n \ , \tag{1}$$

where r_b is the burning rate, P_c is the ambient pressure, a is the burning rate coefficient, and n is the burning rate exponent.

D. Agglomerate Size Determination

Additional samples were burned at atmospheric pressure in front of a long-distance microscopic lens attached to the high speed camera. Images of the regressing burning surface were taken at 3000 frames per second at a 90 μs exposure and a high f-stop to enable examination of the combustion process of the luminous fuel particles. The size of the fuel particles during ignition and subsequent release from the surface was compared with a known scale image, again using GraphClick software. Approximately 250 agglomerates were measured for each propellant sample, and the resulting size data binned, plotted, and curve fitted using either a Gaussian or a log-normal distribution, depending on which was more applicable.

III. Results & Discussion

A. Burning Rate Measurements

The burning rates for propellants A (control), B, and C are shown in Fig. 2. Increasing concentration of the NiAl-forming fuel particles increased the burning rate of the propellant, due to the Ni-Al reaction modifying the structure of the condensed phase thermal wave. Differential thermal analysis (DTA) of the mechanically activated Ni-Al material, conducted previously, indicates an exothermic onset at 473 K.[8] This is significantly lower than the 880 K surface temperature of a typical AP composite propellant,[12] and far lower than the ignition temperature of either neat aluminum or neat nickel powder. As a result, the Ni-Al reaction appears to begin in the condensed phase, effectively raising the subsurface temperature.

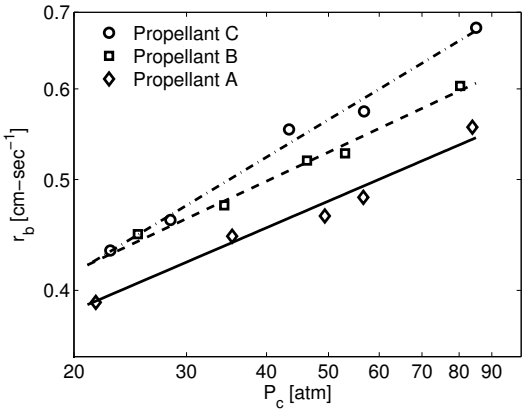


Figure 2: Burning rate data for propellants A, B, and C.

Additionally, the Ni-Al onset temperature is nearly coincident with the temperature of the first endotherm reported during the phase change and combustion process of ammonium perchlorate.[13] Overlaid DTA onset curves for AP and MA Ni-Al are shown in Fig. 3. The resulting interaction of the AP decomposition with the intermetallic exotherm appears to play a significant role in propellant burning rate, as if the burning

rate increase was caused purely by a condensed phase preheat effect, the burning rate exponent would be effectively constant. However, increasing amounts of MA fuel continue to increase the burning rate exponent. Rate parameters a and n are reported for formulations A, B, and C in Table 2.

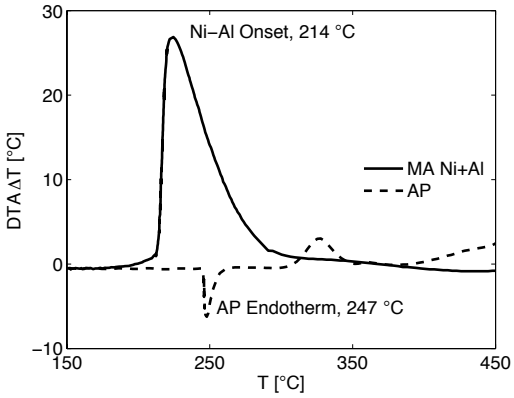
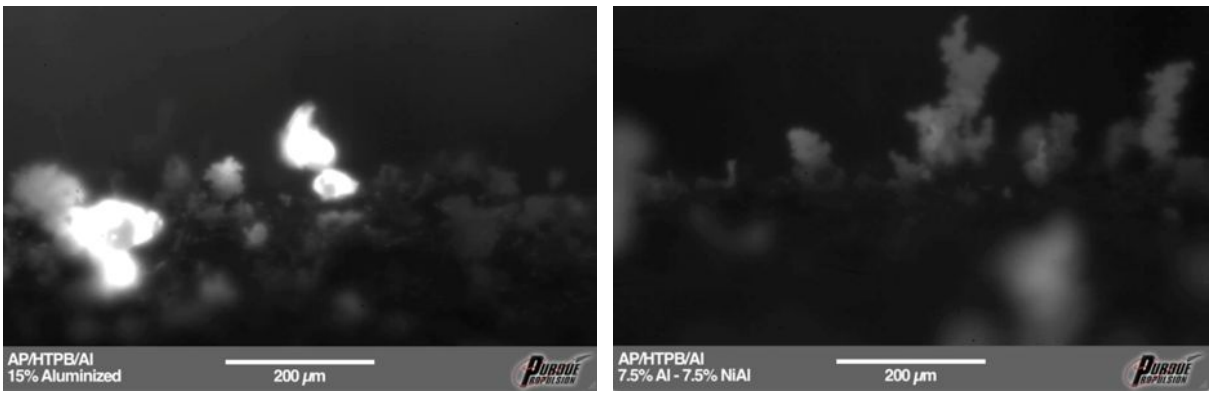


Figure 3: DTA onset curves for MA Ni-Al[8] and AP.[13]

B. Agglomerate Size Measurements



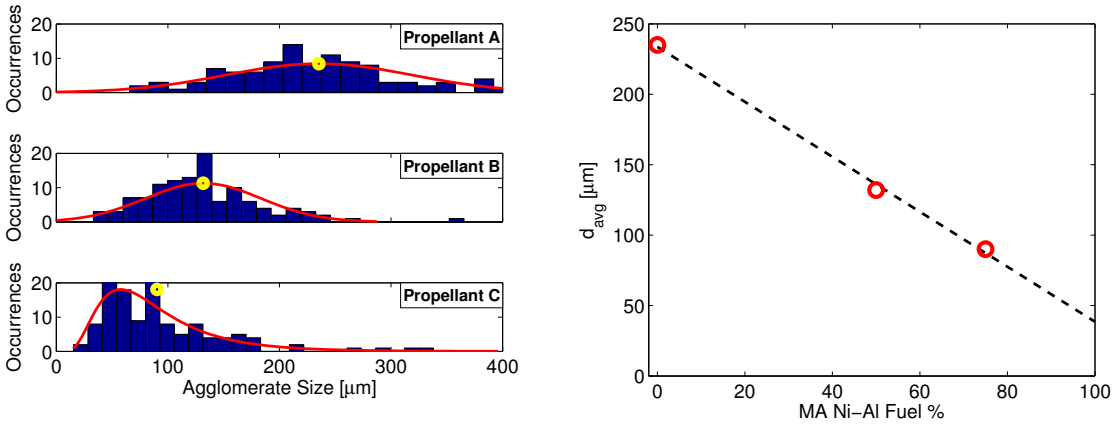
(a) 15 wt.% Al, 0 wt.% Ni-Al (b) 7.5 wt.% Al, 7.5 wt.% Ni-Al

Figure 4: Typical still frames from high-speed microscopic imaging of (a) propellant A and (b) propellants B/C.

Typical images of the agglomerated metal particles during their combustion process are shown in Fig. 4. The distinctly different agglomerate structures are readily apparent; propellant samples without MA material produced large, bright agglomerate droplets, while MA-containing propellants produced thinner, flake-like metal structures prior to releasing from the propellant surface. These flakes were noticeably thinner and more porous than the aluminum droplets in the non-MA containing propellant, and appeared far less luminous.

The agglomerate size distributions measured from each propellant are shown in Fig. 5a, with mean agglomerate diameters reported in Table 2. Propellants A and B are fit with Gaussian curves, as their mean distribution values lie very close to the mode of the data distribution. Propellant C exhibits a more log-normal particle size distribution, which is a typical feature of materials undergoing condensed-phase agglomeration.[14] The overall trend is that of decreasing particle diameter with increasing Ni-Al addition, suggesting that the addition of the MA Ni-Al may provide an increase in performance. Mean agglomerate size as a function of MA Ni-Al fuel content (ranging from 0% – pure Al – to 100% MA Ni-Al) appears to be a linear function, as shown in Fig. 5b.

One potential pitfall to this method of measuring agglomerate size is that the dynamic fluid environment present in the chamber of a solid rocket motor is not well simulated. During actual motor operation, the



(a) (b)

Figure 5: (a) Agglomerate size distribution and (b) mean agglomerate size as a function of Ni-Al fuel content for propellants A, B, and C.

particle residence time may be long enough (and the port volume crowded enough) that the porous flake-like structures may collide with one another and agglomerate prior to entering the nozzle region, thus negating the efficiency benefit derived from the minimization of two-phase flow. However, since these flakes are created at significantly smaller sizes than the agglomerates of the baseline propellant, there is a good chance that an increase in efficiency may ultimately appear.

Table 2: Empirical burning rate parameters a and n and mean agglomerate sizes d_{avg} for tested propellants.

Propellant	a [cm-sec^{-1}-atm^{-n}]	n	d_{avg} [μm]
A	0.187	0.240	235
B	0.190	0.262	132
C	0.151	0.337	90

IV. Conclusion

Mechanically activated intermetallic forming compounds were added to AP/HTPB composite propellants in an effort to reduce metal particle agglomerate size and increase burning rate. Burning rates at 68.04 atm were increased from 0.515 cm/sec to 0.574 cm/sec with the replacement of 50 wt.% Al with MA Ni-Al, and to 0.626 cm/sec with the replacement of 75 wt.%. Mean agglomerate size was decreased markedly, from 235 μm for the baseline propellant, to 132 μm and 90 μm for propellants containing 50 wt.% and 75 wt.% replaced fuel, respectively. The agglomerate size continues to decrease linearly with continued MA material addition.

The Ni-Al system chosen for this work presents the somewhat significant drawback of adding nickel to the exhaust species. Since the molecular weight of Ni is relatively high, this causes a deficit in delivered specific impulse when compared to solely Al-containing propellants, especially in the higher quantities necessary for significant agglomerate size reduction. The Ni-Al system was chosen for this work primarily due to the deep experience of this group with Ni-Al; potentially more suitable intermetallic systems for propellant use include titanium/boron and titanium/carbon. The titanium/boron and titanium/carbon systems, especially, may sufficiently mitigate the I_{sp} deficit so as to provide a net increase in motor performance.

Thus, a wise starting point for future work would be the further development and characterization of propellants containing various higher performance intermetallic forming compounds as fuels. Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) of reaction onset with ammonium perchlorate would prove useful to determine the effect on decomposition provided by the simultaneous en-

dotherm/exotherm noted for AP and Ni-Al. Measurements of agglomerate size at increased ambient pressure would also be wise, as these measurements would more closely match the operating conditions of a rocket motor chamber. Perhaps the most telling experiment would be to cast a series of small rocket motors using intermetallic fuel compounds and measure their performance efficiency during hot fire testing. A tremendous amount of work remains to be done to explore the possibilities of intermetallic forming compounds as fuels for composite rocket propellants and understand the impact they may have on solid rocket motor performance.

Acknowledgments

The authors would like to acknowledge J. E. Moore and R. V. Reeves for their work in developing, preparing, and characterizing the Ni-Al material.

References

[1]Davenas, A., editor, *Solid Rocket Propulsion Technology*, Pergamon Press, New York, 1993.

[2]Geisler, R., "A global view of the use of aluminum fuel in solid rocket motors," *Proceedings of the 38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, Vol. 3748, 2002, pp. 2002.

[3]Gallier, S., "A Stochastic Pocket Model for Aluminum Agglomeration in Solid Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 34, No. 2, April 2009, pp. 97–105.

[4]Hermsen, R. W., "Aluminum Oxide Particle Size for Solid Rocket Motor Performance Prediction," *Journal of Spacecraft and Rockets*, Vol. 18, No. 6, 1981, pp. 483–490.

[5]Yetter, R., Risha, G., and Son, S., "Metal particle combustion and nanotechnology," *Proceedings of the Combustion Institute*, Vol. 32, No. 2, 2009, pp. 1819–1838.

[6]Dokhan, A., Price, E. W., and Seitzman, J., "The effects of bimodal aluminum with ultrafine aluminum on the burning rates of solid propellants," *Proceedings of the Combustion Institute*, 2002, pp. 2932–2945.

[7]White, J. D. E., Reeves, R. V., Son, S. F., and Mukasyan, A. S., "Thermal Explosion in Al-Ni System: Influence of Mechanical Activation," *Journal Of Physical Chemistry A*, Vol. 113, No. 48, 2009, pp. 13541–13547.

[8]Reeves, R. V., *Control of Ignition and Reaction Behavior in Gasless Reactive Systems via Microstructural Modification*, Ph.D. thesis, Purdue University, May 2011.

[9]Yan, A. H., Jackson, T. L., Son, S. F., and Venugopal, P., "Validation of Numerical Simulations for Nano-Aluminum Composite Solid Propellants," *Journal of Propulsion and Power*, Accepted May 10, 2011.

[10]ResoDyn Corporation, Butte, MT, USA, *LabRam ResonantAcoustic Mixer Manual*.

[11]Arizona Software, Neuchâtel, Switzerland, *GraphClick Manual*.

[12]Selzer, H., "The Temperature Profile Beneath the Burning Surface of a Composite Ammonium Perchlorate Propellant," *Eleventh Symposium (International) on Combustion*, 1967, pp. 439–445.

[13]Ma, Z., "Effect of Fe2O3 in Fe2O3/AP Composite Particles on Thermal Decomposition of AP and on Burning Rate of the Composite Propellant," *Propellants, Explosives, Pyrotechnics*, Vol. 31, No. 6, Dec. 2006, pp. 447–451.

[14]Bakrania, S., Miller, T., Perez, C., and Wooldridge, M., "Combustion of multiphase reactants for the synthesis of nanocomposite materials," *Combustion and Flame*, Vol. 148, No. 1-2, 2007, pp. 76–87.