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# Ignition and combustion behavior of mechanically activated Al–Mg particles in composite solid propellants

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ABSTRACT

Metallized propellants typically produce large agglomerates that result in two-phase flow losses. Tailoring composite metal fuel particles can improve ignition and combustion characteristics while reducing product droplet sizes. In this work, mechanically activated (MA) aluminum (Al) and magnesium (Mg) powders are synthesized, characterized and compared to magnalium (Mag) alloy, neat Al, neat Mg and their physical mixtures (PM) at the same 1:1 mass ratio as MA and Mag powders. $CO_2$ laser ignition tests showed that the MA powders are more reactive than those of Mag and exhibit particle fragmentation upon ignition. Mag powders only show fragmentation and microexplosions at high heating rates. The burning rates of the ammonium perchlorate/hydroxyl-terminated polybutadiene composite propellants containing MA powders were the highest, compared to Mag, neat Al, PM and neat Mg in decreasing order. High-speed imaging of the propellants and product collection showed that MA, Mg and Mag powders produce much smaller agglomerates than neat Al or PM at lower pressures due to fragmentation and Mg vaporization. However, the microexplosion tendency of the MA and Mag particles in the propellants was reduced at higher pressures due to reduced vapor bubble growth. Out of all the materials investigated, MA particles provide the best combination of burning rate and product sizes.



## 1. Introduction

Aluminized propellants typically produce large agglomerates that can significantly affect the performance of small to medium size rocket motors due to two-phase flow losses, accounting as much as 10% reduction in specific impulse ($I_{sp}$) [1]. The accumulation of slag can also be a significant concern. The aluminum (Al) particles tend to melt and coalesce on the propellant surface due to relatively slow ignition rates. In order to reduce the losses, Al particles should be tailored to ignite easily at or near the propellant surface, or break into smaller particles *in-situ*.

Different methods have been proposed to reduce agglomeration in aluminized solid propellants either by using smaller Al particles like nano-aluminum (nAl) [2], metallic coatings such as nickel (Ni) [3], polymeric coatings [4] or other inclusions [5–8]. The problem with nAl is that it decreases propellant specific impulse as nAl can contain 10–25 wt.% aluminum oxide [2] and can result in poor propellant rheology and aging [9]. Metallic and polymer coatings result in decreased agglomeration sizes in comparison to neat Al but still about five times larger than the initial particle size [10]. Inclusions such as Ni require large amounts to have reasonable agglomeration reduction and the higher molecular weight products can significantly reduce the performance.

The concept of microexplosion as a means to break-up fuel drops was first identified by Ivanov in 1965 [11]. It was recognized that the occurrence of microexplosion can be due to the difference in volatility between two or more liquid components. Lighter more volatile components within a multi component droplet are trapped inside a shell of the heavier less volatile component and are superheated with increased heat diffusion. They form bubbles which grow until reaching a critical size that causes the whole droplet to explode. Microexplosion phenomena was extensively studied in liquid fuels in either miscible fuel mixtures [12] or water/oil emulsions [13]. As a result, it was realized that microexplosion phenomena could be utilized to enhance atomization in diesel engines [14]. It was also identified that microexplosion has a stochastic nature and cannot be predicted by the classical criterion of superheat limit and droplet temperature. This probability was shown to be controlled by droplet lifetime and nucleation time, with the probability decreasing with a decrease in the initial droplet diameter [15].

In contrast to liquid fuels, little attention was paid to microexplosion phenomenon in metal/alloy combustion. It was only

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noted as a side observation for magnesium (Mg) [16] and Al [17]. Breiter et al. [18] reported microexplosion of Al–Mg alloy particles in the flame of oxidizer–fuel mixture. They found that the probability of microexplosion reached a maximum at eutectic composition. Blackman and Kuehl [19] reported microexplosion in Al–Mg and Al–Li particles, with the larger probability of microexplosion in Al–Mg particles. More recently, Terry et al. [20,21] have shown that a 1:1 molar Al–Li alloy will microexplode in a solid propellant and promises improved theoretical $I_{sp}$ and reduced HCl production.

One alternative method to synthesize metal composites and alloy particles with higher reactivity is mechanical activation. The resulting particles exhibit nanoscale mixing with large interfacial areas that increase reaction rates [22,23]. For example, particles of Al and Mg that have been mechanically activated (MA) have lower ignition temperatures compared to their original constituents during their combustion as aerosols [24] and in hydrocarbon flames [25]. Such particles also exhibit fragmentation and can be used as a metal fuel in solid propellants. Sippel et al. have examined MA of Al with non-metal inclusions [6–8], and Rubio et al. showed that such composite particles can microexplode under $CO_2$ laser heating [26], but MA of multiple metal systems, with comparisons to alloys or physical mixes, needs more study.

The objective of this research is to synthesize and characterize composite metal fuels that exhibit microexplosion phenomena and exploit this for product size reduction in solid propellants for enhanced performance. The particles used were neat Al and Mg, MA mixtures of Al and Mg at a 1:1 mass ratio using a planetary mill, as-purchased magnalium (Mag), an Al–Mg alloy at the same overall composition as well physical mixtures (PM).

## 2. Experimental

Starting materials are Mag (C160BM FireFox Inc. −200 mesh), elemental powders of Al (Alfa Aesar, 99.8% pure, −325 mesh) and Mg (Alfa Aesar, 99.8% pure, −325 mesh). Powders were mechanically milled using a Retsch PM-100 planetary mill. Nominal powder composition was 1:1 for Al:Mg by mass. The rotational speed was set to 200 revolutions per minute (rpm). The direction of rotation was set to reverse every 15 min. Preliminary laser ignition tests for sieved particles showed that most of the particles are loose aggregates that quickly pulverize under heating. Therefore a second milling step was introduced to break the loose aggregates further. This second milling step was performed using US Stoneware (CV-90116) roller mill with 125 ml HDPE container (VWR-414004-156) for 4 h. A charge ratio of 70 was used with 4.76 mm (McMaster-Carr 9529K13) 440 steel media. Prior to incorporation in laser ignition or propellants, the powders after the two-step process were dry sieved to a range of 25–75 µm.

Powder morphology and elemental distribution inside the particles was investigated using FEI Nova 200 Dual Beam scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). Phase compositions of the powders were analyzed using X-ray Diffraction (XRD) Bruker D8 Focus diffractometer with 5 deg/min scan rate. Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (TA Instruments Q600 SDT) of 0.6–3 mg samples of sieved Mag powders and MA powders was performed over a temperature range of 100–1000 °C at a heating rate of 20 °C/min under 100 mL/min flow of a 20/80 vol.% Oxygen/Argon ($O_2$/Ar) gas mixture.

Loose powder ignition was performed using a $CO_2$ laser (Coherent GEM 100A) with a setup similar to the one reported in [27]. $CO_2$ laser beam was directed to the sample through a series of mirrors and was focused with a ZnSe lens with a focal length of 500 mm to get varying irradiance levels to measure the ignition delays. The powders were placed on square porcelain tiles (25.4 × 25.4 mm) and ignited at varying irradiance levels. The ignition and combustion was observed using high-speed Schlieren imaging (Phantom V7.3, Vision Research) at 10,000 frames/s (fps). The Schlieren system (Edmund Optics, 71-013) featured two aluminized spherical 152.4 mm diameter mirrors with 1524 mm focal distance. The LED from the kit was replaced with a higher power unit to improve the contrast (www.ledsupply.com, CREEXPE2-COL-X with a 20 mm Narrow Spot LED Optic, model 10,003).

Propellants consisted of 14 wt.% of a hydroxyl–terminated polybutadiene (HTPB) binder cured with isophorone diisocyanate (IPDI), 71 wt.% ammonium perchlorate (AP) (80 wt.% coarse 200 µm and 20 wt.% fine 20 µm, ATK), and 15 wt.% of the metal fuel. The metal fuels used were neat Al, neat Mg, PM of Al and Mg, MA Al–Mg and Mag. The mixing procedure is similar to [8]. The propellants were burned at pressures in the range 0.1-6.9 MPa in Ar environment.

The ignition of metal particles at the propellant burning surface was observed at ambient conditions using a high-speed video camera (Phantom v7.3) at 10,000 fps with a macro lens (Nikkor AF Micro 105 mm) and a microscopic lens (K2 infinity). Propellant products were collected using the same procedure in [8], where a borosilicate disc attached to a motorized swinging arm was moved across the plume at a speed of 7 m/s at a distance of 5 mm from the burning surface. The images were acquired using an optical microscope (Hirox KH-8700) and analyzed using ImageJ software.

## 3. Results and discussion

### 3.1. Particle morphology

Figure 1 shows SEM images of the powders. The first and second columns are the spherical Al and spherical Mg powders, the third column shows equiaxed but jagged Mag particles while the fourth column shows the MA powder. Mag at this composition consists of brittle intermetallic phase $Al_{12}Mg_{17}$. The MA powder appears to have more flake-like morphology with average thicknesses on the order of 5 µm. This is typical of MA powders, which tend to flatten due to repeated compression and plastic deformation between impacting steel balls that have much larger diameters.

### 3.2. Particle composition

The internal distribution of elements inside Mag and MA powders was investigated using Focus Ion Beam (FIB) in the FEI Nova 200 Dual Beam SEM. The Mag particles showed a homogenous elemental distribution as expected (Fig. 2(a)). Low magnification EDS maps showed that MA particles exhibit large compositional deviations from the bulk composition (52.6 at.% Mg). After investigating multiple particles, it was concluded that the MA powders are more like a physical mixture of Al-rich particles (Al may reach 90 at.%) and Mg-rich particles (Mg may reach 95 at.%). Moreover, the average Mg content was 60 at.%. Additional EDS on smaller MA particles (<25 µm) showed that they were more homogenous than the larger size range with a lot more mechanical mixing compared to their larger counterparts. Their overall Mg content was 35 at.%. This implies that both the microstructure as well as average composition varies as a function of particle size in MA particles and can significantly deviate from nominal values for the milling settings employed. It is possible that higher milling rotation rates or longer milling durations could produce more uniform compositions.

### 3.3. Phase composition (XRD)

XRD patterns for both Mag and MA powders are shown in Fig. 3. For the MA powder, the pattern shows only peaks of Al and