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Modifying burning rate and agglomeration size in aluminized composite solid propellants using mechanically activated metals

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MODIFYING BURNING RATE AND AGGLOMERATION SIZE IN ALUMINIZED COMPOSITE SOLID PROPELLANTS USING MECHANICALLY ACTIVATED METALS

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This dissertation is dedicated to
my lovely wife Reham:
For sacrifice of her youth to stand with me

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Finally, I would like to thanks the poor Egyptian people who with their sweat and blood contribute to fund me during my fellowship, I pray to God that I can pay them back and help making their live better and their future better.

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ABSTRACT

Belal, Hatem Mohamed. Ph.D., Purdue University, December 2016. Modifying Burning Rate and Agglomeration Size in Aluminized Composite Solid Propellants using Mechanically Activated Metals . Major Professors: Steven F. Son, School of Mechanical Engineering, and Volkan Ortalan, School of Material Science.

Agglomeration reduction techniques are important field in solid propellant industry, Large agglomeration results in excessive two phase losses. Tailored composite particles has been applied to tailor aluminum particle ignition and combustion. In this research, mechanical activated aluminum magnesium powders are synthesized, tested in both laser ignition using CO2 and propellant. Prepared powders categorized into particle size that suitable for propellant application. Laser ignition tests showed that the prepared powder are more reactive than magnalium which has the same Al:Mg weight ratio. Agglomeration capturing showed that the prepared powder produce much less than neat aluminum or even similar physical mixture of aluminum and magnesium. The burning rate of propellant using the prepared powder is increased.

MA Al/Mg powders as long as with comparable physical mixture are applied in propellant formulation with AP/HTPB. In order to quantify the effect of changing Mg percent. Burning rate is measured from videos captured for strand burning in windowed pressure vessel, also the agglomeration was capturing using special setup. The results showed that MA powder increase burning rate and this increase reach maximum at 50% Mg, while propellant using physical mixture of Al/Mg show constant or little decrease in burning rate. In addition, the MA powder show lower agglomeration size in comparison to neat aluminum propellant or physical mixture with the same Mg percent. The lowest agglomeration sizes were for MA50. However, equilibrium calculation showed 4 sec losses

in specific impulse, so MA 70 was chosen as a compromise between low agglomeration size at the minimum loss in specific impulse.

Magnalium is an alloy of aluminum and magnesium and it is known for its ease of ignition and high oxidation energy content. It has been used as a metal fuel to increase burning rates of composite modified double base (CMDB) and ammonium perchlorate (AP) composite propellants. However, the ignition temperature is larger than the comparable mechanically activated (MA) Al-Mg powder.

Mechanical milling was performed on magnalium powders and modifications of structure and morphology of the alloy during milling were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The prepared magnalium powder was used in a solid propellant, which showed higher burning rates than those containing as-received magnalium. Furthermore, milled magnalium showed higher agglomeration reduction than both as received magnalium as well as MA Al-Mg powders.

Extend the application of mechanical alloying of aluminum to other metals with extreme difference in melting/ boiling temperature, the first is Zirconium which is a long time candidate in solid propellant community. The ease of zirconium ignition and the micro-explosive behavior shown by neat zirconium particles promote its usage in agglomeration reduction effort. the other metal is Indium, which has very low melting point compared to other metal, this may open the possibility of earlier reaction of aluminum particles at or near propellant surface resulting in less pre ignition time which reduce agglomeration tendency.

MA of 90% Aluminum and 10% of Zirconium or 10% Indium using High energy ball milling, particle characterization using SEM/FIB, XRD and DSC/TGA are performed, burning rate and agglomeration size analyses of solid propellant using sieved MA-powder are done. The results showed that the both MA Al-ZR and MA Al-In ignite in laser beam which verify change in reactivity from neat aluminum with its protective alumina coating. However, burning rate results show no change in burning rate from neat aluminum, also the prepared material shows no reduction in agglomeration sizes

CHAPTER 1. INTRODUCTION

1.1 Motivation

Agglomeration reduction has been an objective for most of workers in solid propellant industry for decade. Because of the protective coat of aluminum oxide over the surface of aluminum, aluminum particles melt and coalesce before ignite far from surface. This results in formation of large product agglomerate. These large agglomerate are responsible in significant two phase losses. In order to reduce these two phase losses, aluminum particles should be tailored to ignite easily near or at propellant surface, or burning into smaller particles.

Different ways have been proposed to reduce size of agglomeration in aluminized solid propellant either by using smaller aluminum size (e.g. nano-aluminum nAl [2]), metallic coating (nickel [3]), polymeric coating [4] or other metal inclusion [5]. The problem with nAl is that decreases propellant specific impulse, as nAl can contain 10 to 25 wt.% aluminum oxide [2] and can result in poor propellant aging [6]. The metallic coating results in decrease agglomeration size in comparison to neat Al but still about five times larger than the initial particle size [7]. The polymeric coating suffers from the same problem. Nickel inclusion has been tried but it requires large nickel inclusion to have reasonable agglomeration reduction.

On the contrary to liquid fuels, Little attention was paid for microexplosion phenomenon in metal/alloy combustion. It was considered as a side observation. Law [13] reported microexplosion in neat magnesium, Microexplosion in Al [14]. Breiter et al. [15] reported microexplosion of Al-Mg particles in the flame of oxidizer-fuel mixture. They found that the probability of microexplosion is maximum at eutectic composition.

Blackman and Kuehl [16] reported microexplosion in Al-Mg and Al-Li particles, with the larger probability of microexplosion in Al-Mg particles.

1.2 Objective

The objectives of this research were as follows:

Extend the concepts of microexplosion into solid propellant industry by testing as received particles and /or synthesis composite particles that satisfy the criteria for micro-explosion stated for liquid fuels.

Quantify the effects of changing the composition of such particles on agglomeration reduction

Quantify the effects that mechanical milling has on particles characteristics and the effect of these characteristics on burning rate / agglomeration size

1.3 Document Organization

Chapter one of this dissertation provides a brief motivation for the work and describes the organization of the document. Chapter two describes in detail the synthesis of mechanical activated Al Mg particles with weigh ratio 1:1 as well as their characteristics (size, morphology, and oxidation characteristics,) using SEM, EDS, DSC/TGA and XRD. The third chapter discuss the effect of variation of magnesium percent on characteristics of MA Al-Mg composite particles with the effects it has on burning rates and agglomeration reduction efficiency. Chapter four of this document Mechanical milling for al-Mg intermetallic(magnalium) and how mechanical milling of such brittle material can enhance burning characteristics and the overall effect on enhancing burning rate. Chapter five deals with different metal inclusion (Indium and Zirconium), procedure to synthesis these MA powders, and characteristics of these material with their effects on burning rate and agglomeration size reduction,

CHAPTER 2. BEHAVIOR OF MECHANICALLY ACTIVATED ALUMINUM-MAGNESIUM PARTICLES IN COMPOSITE SOLID PROPELLANTS

2.1 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 (Isp) [1]. The aluminum (Al) particles tend to melt and coalesce on the propellant surface due to relatively slow ignition rates and this results in formation of large products. 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 ways 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 metal inclusions [5]. The problem with nAl is that it decreases propellant specific impulse as nAl can contain 10 to 25 wt.% aluminum oxide [2] and can result in poor propellant aging [6]. The metallic coating results in decreased agglomeration sizes in comparison to neat Al but still about five times larger than the initial particle size [7]. The polymeric coatings suffer from the same problem. Ni inclusion has been tried but it requires large Ni amounts to have reasonable agglomeration reduction and the higher molecular weight products further reduce the performance.

The concept of microexplosion as a means to break up fuel particles was first identified by Ivanov in 1965 [8]. It was recognized that the occurrence of microexplosion is due to the difference in volatility between two or more liquid components. Lighter components within a multi component droplet are trapped inside a shell of the heavier 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 mixture [9] or water/oil emulsions [10]. As a result, it was realized that microexplosion phenomena can be utilized to enhance atomization in diesel engines [11]. 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 [12]

Contrary to liquid fuels, little attention was paid to microexplosion phenomenon in metal/alloy combustion. It was only considered as a side observation for magnesium (Mg) [13] and Al [14]. Breiter et al. [15] reported microexplosion of Al-Mg particles in the flame of oxidizer-fuel mixture. They found that the probability of microexplosion is maximum at eutectic composition. Blackman and Kuehl [16] reported microexplosion in Al-Mg and Al-Li particles, with the larger probability of microexplosion in Al-Mg particles.

The objective of this research is to synthesize and characterize composite metal fuels that exhibit microexplosion phenomena and exploit this in product reduction in solid propellants for possible enhanced performance. The particles used were mechanically activated (MA) mixtures of Al and Mg at a 1:1 mass ratio using a planetary mill, or as-purchased magnalium, an Al-Mg alloy at the same overall composition. The particles were characterized using microscopy and thermal analysis and were ignited using a CO2 laser and imaged at high-speed. The propellants containing the powders were investigated for burn rates and particle collection was performed to assess the break-up of the products.

2.2 Experimental Methods

Material Synthesis

Starting materials included magnalium (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 MA 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 minute (min). The preliminary laser ignition tests for sieved particles showed that the particles consisted of loose aggregates and a second milling step is introduced to break them up further. This second milling step is performed using US Stoneware (CV-90116) roller mill with 125 ml HDPE container (VWR-414004-156) for 4 hours (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 ranges between 25 and 75 µm and less than 25 µm.

Methods

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) . The size distributions of the sieved MA composite powder as well as similarly sieved reference powders of spherical (Valimet H30) and magnalium were verified using a Malvern Mastersizer 2000 with Hydro 2000 lP dispersion unit with isopropyl alcohol as the medium. Phase compositions of the powders were analyzed using X-ray Diffraction (XRD) Bruker D8 Focus diffractometer with 5 deg/min scan rate. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of 1-3 mg samples of sieved magnalium powders, milled powders and physical mixtures was performed with a TA Instruments Q600 SDT over a temperature range of 100-1000oC at a heating rate of 20 °C /min under a 100 mL/min flow of a 20/80 vol.% O2/Ar gas mixture.

Loose powder ignition is performed using CO2 laser (Coherent GEM 100A) with a setup similar to the one reported in [17]. The CO2 laser beam is directed to the sample through a series of mirrors and is focused with a ZnSe lens with a focal length of 500 mm to get different irradiance levels.

Propellants consisted of 14 wt.% of a hydroxyl-terminated polybutadiene (HTPB) binder cured with isophorone diisocyanate (IPDI), 71 wt.% 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, physical mixture of Al and Mg (PM 50), MA Al-Mg and magnalium.

The mixing procedure is similar to [18]. The propellants were burned at various pressures in the range 0.1- 6.9 MPa in Ar and N2 gas environments.

The ignition of metal particles at the propellant burning surface was observed at 1 atm pressure using a high-speed video camera (Vision Research, Phantom v7.3) at 10,000 frames/s (fps). Propellant products were collected and analyzed using the same procedure in [18].

2.3 Results and discussion

Particle morphology and dimensions

Figure 1 shows SEM images of the used powders. The first and second columns show the spherical Al and spherical Mg powder, the third column shows equiaxed but jagged magnalium particles while the fourth column shows the mechanically activated (MA) powder. The MA powder appears to have flake-like morphology with average thicknesses on the order of 5 µm, which is similar to flake aluminum discussed in [18].

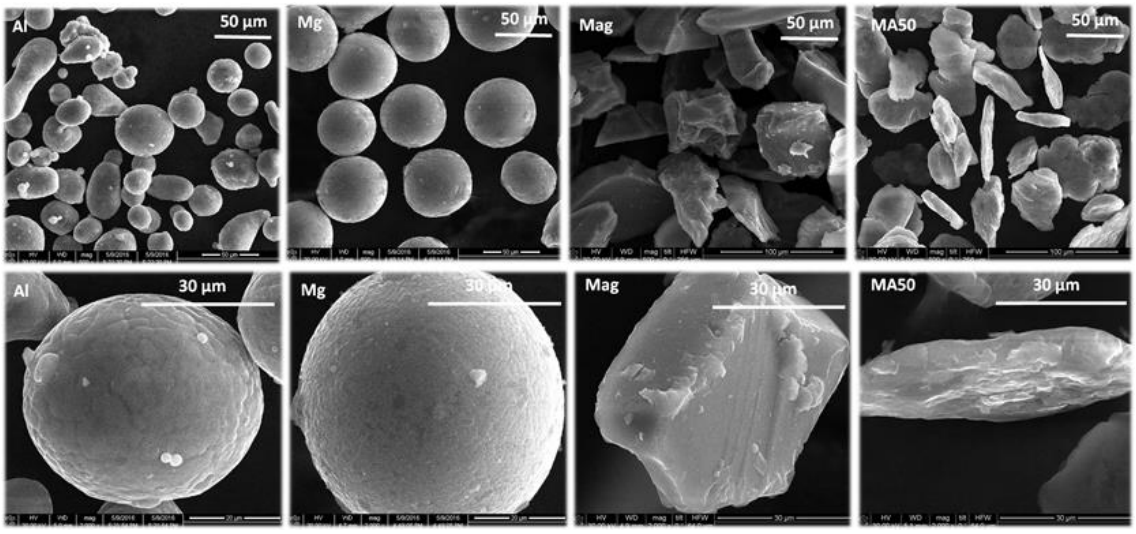

Fig. 1 SEM images of Al, Mg, magnalium (Mag) and MA powders

Measured size distributions (Fig. 2) show that a small portion of the milled powder is outside the nominal sieve dimensions (25-75 µm which are shown as vertical dashed lines in Fig. 2). However, for the case of magnalium powder, there was a large portion larger than 75 µm. These might be due to particle morphologies with large aspect ratios that allow large particles to pass through sieves.

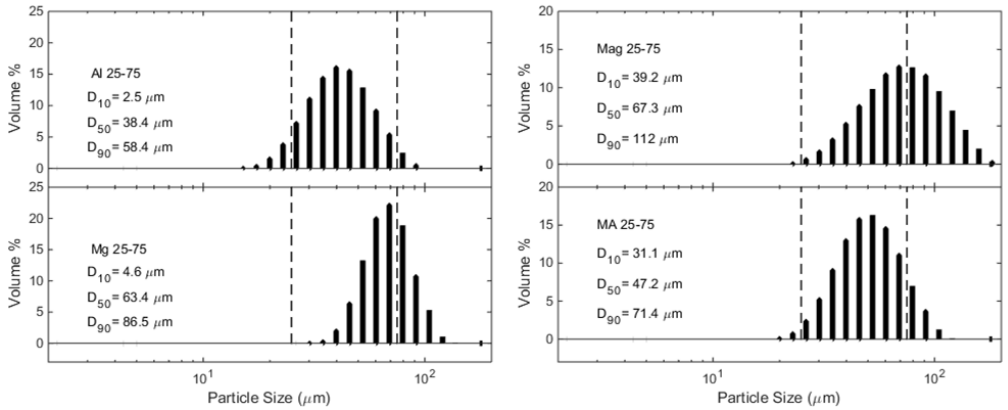

Fig. 2 Particle size distribution for neat elements Al, Mg (left) and magnalium (Mag) and MA powders (right)

Particle Composition

The internal distribution of elements inside magnalium and MA powders is investigated using Focus Ion Beam (FIB) capability in the FEI Nova 200 Dual Beam SEM. The magnalium particles showed a homogenous elemental distribution as expected (Fig. 3).

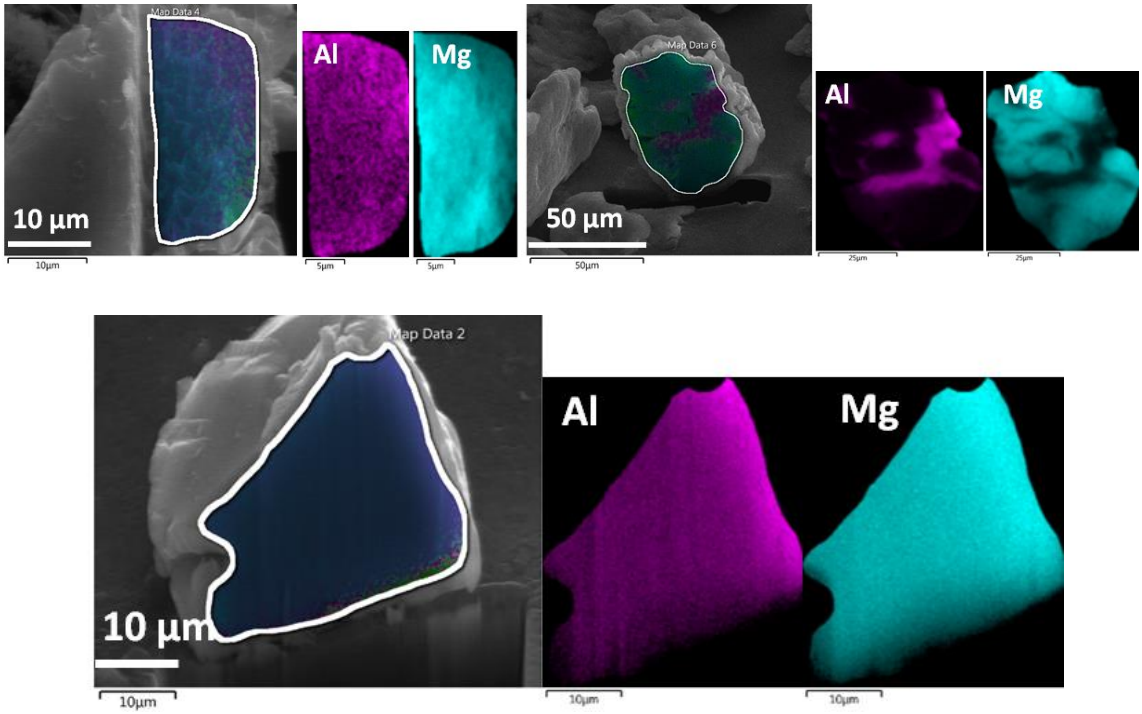

Fig. 3 EDS maps for the used powders above left: MA D<25 μm, above right: MA 25<D<75 μm lower row: magnalium particles.

However, MA particles showed that particles in the small size range (<25 μm) are more homogenous than the larger size range. Also, low magnification EDS maps showed that the particles exhibit large compositional deviations from the bulk composition, with variations from particle size range to another: the average magnesium content in the small particle size range (i.e. D<25) is 35 % while in the large size range (i.e. 25<D<75 μm), it is 60%. Investigating different particles, it is concluded that the MA powders are more like a physical mixture of Al-rich particles (Al may reach 90%) and Mg rich particles (Mg % may reach 95%). This implies that not only microstructure but average composition varies as a function of particle size in MA particles and can significantly deviate from nominal values. Smaller particle tends to show a lot more mechanical mixing compared to their larger counterparts

Phase Composition (XRD)

XRD patterns for both magnalium and MA powders are shown in Fig. 4. For the MA powder, the pattern shows only peaks of Al and Mg, indicating that there is no significant interaction (diffusion, etc) between the constituents during mechanical activation. The magnalium powder shows only peaks of Al12Mg17 intermetallic phase as expected from this overall composition.

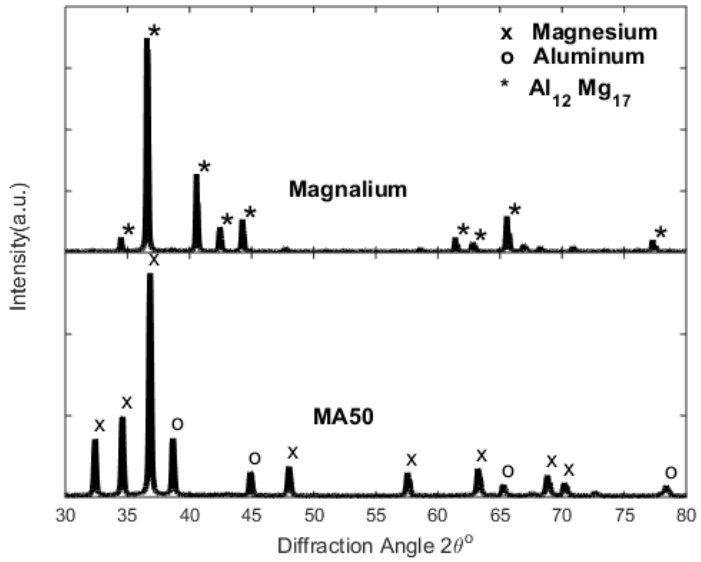

Fig. 4 XRD patterns of magnalium and MA powders.

Thermal Analysis

DSC measurements were performed in Oxygen-Argon environment (20% O2, 80%Ar) to observe how the particles react and oxidize. Figures 5 and 6 show the DSC-TGA results for MA and magnalium particles less than 25 µm and in the range 25-75 µm respectively. The magnalium particles show a melt endotherm at around 450°C, which is the melting point of magnalium (Al12Mg17) as in Al-Mg binary phase diagram [19]. The smaller particles started oxidizing at lower temperatures (540 °C) compared to the larger ones. The total reaction heat was similar for both at around 10.7 kJ/g. The weight gain was around 75%, close to the theoretical value for the case of complete oxidation (77.4%) assuming the formation of Al2O3 and MgO. This indicates that the particles were most probably completely oxidized.

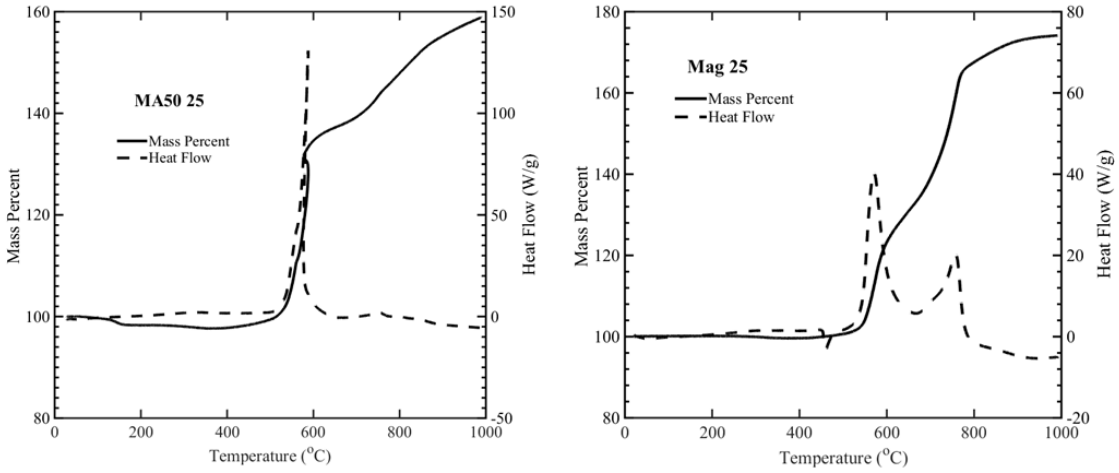

Fig. 5 DSC/TGA from 100-1000°C (20 °C /min, 20/80 vol% O_2/Ar) of (a) MA and (b) magnalium (Mag) powders sieved to less than 25 µm.

MA powders showed no endothermic peak, which suggests that very little diffusion or reaction occurred during milling that might form the Al12Mg17 intermetallic phase, which is in agreement with FIB and XRD results. Reaction starts at (540 °C) as in the case for magnalium but at very high rates. Larger particles had a secondary reaction, whereas the smaller ones reacted in one step. The weight gain was 60% due to oxidation, which was less than magnalium. This might be due to the fact that the MA particles have relatively large microscale sections that are Al-rich as seen in EDS maps in Fig. 3. Diffusion limited

growth can limit the oxidation rates in the temperature range investigated to prevent complete oxidation. The reaction heat for the large MA particles was similar to magnalium at around 11 kJ/g, but it was lower for the finer particles, 7.5 kJ/g. However, the reaction goes fastest for these particles and it is very plausible that the DSC underestimates it as the self-heating rates are too high. This is evident from the heat flow curves, which show sharp peaks when the reactions proceed rapidly. Therefore, the integrated heats reported here represent the minimum values.

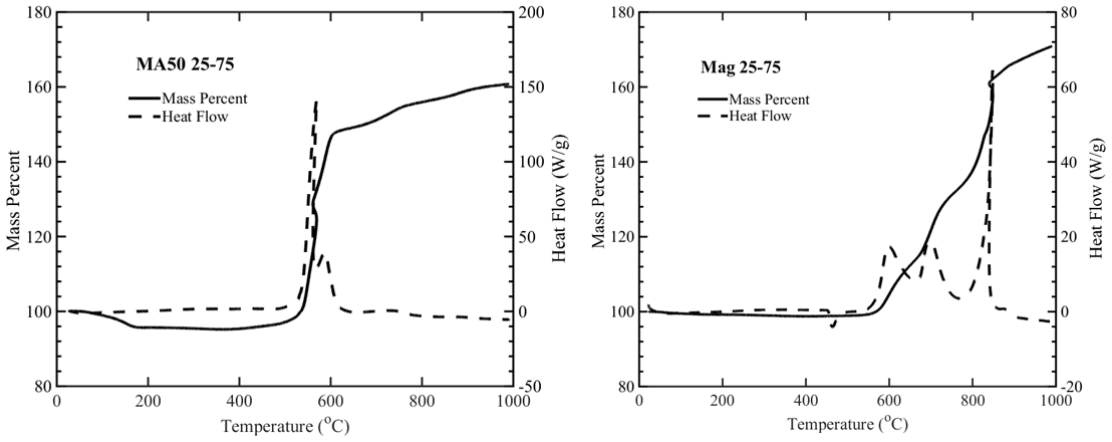

Fig. 6 DSC/TGA from 100-1000°C (20 °C /min, 20/80 vol% O_2/Ar) of (a) MA and (b) magnalium (Mag) powders sieved to between 25-75 µm.

Loose Powder Ignition

The ignition durations for the loose particles are shown in Fig. 7. The setup was identical to that used in [17], where powders are placed on a porcelain tile and ignited using a CO2 laser at varying irradiance levels. The results show the differences between the reactivity of magnalium and MA particles in air.

The ignition delay for MA was lower than magnalium in both size ranges and indicating that they are significantly more reactive due to the high degree of microstructural refinement, typical in MA materials. However, for the small size range, the difference decreased with increased peak incident irradiance. For large size range, the difference was similar even at high peak irradiances.

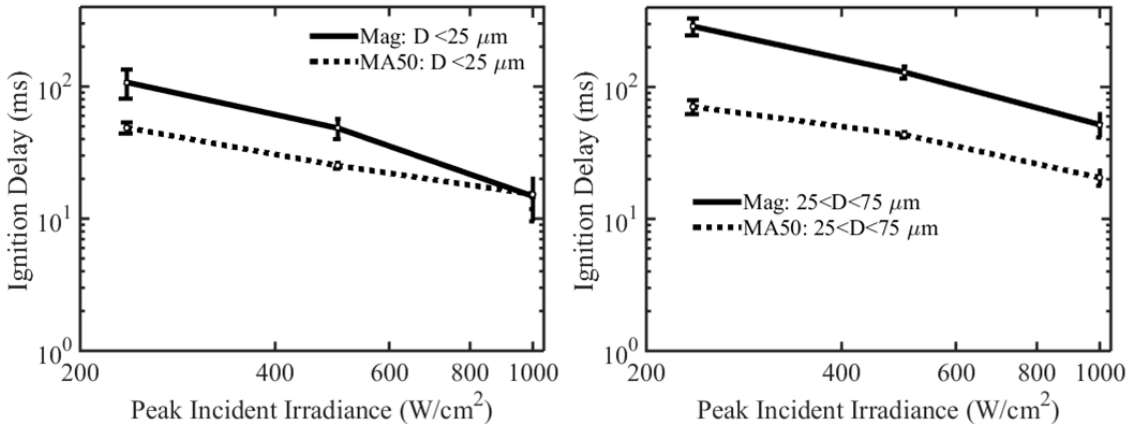

Fig. 7 Ignition delay time for magnalium (Mag) and MA powders. Left: particles < 25 µm, Right: particles sieved between 25-75 µm

Propellant Combustion

Images of propellants burning at 0.1 MPa (Fig. 8) show that the metal fuels behave differently both at propellant surface and in gas flow. For the propellant with neat Al, very little Al ignition is observed at the surface and most of the combustion begins only after particles have traveled about 4 mm from the propellant surface. This results in a dark region near the burning surface of the propellant, where particles tend to melt and form agglomerates.

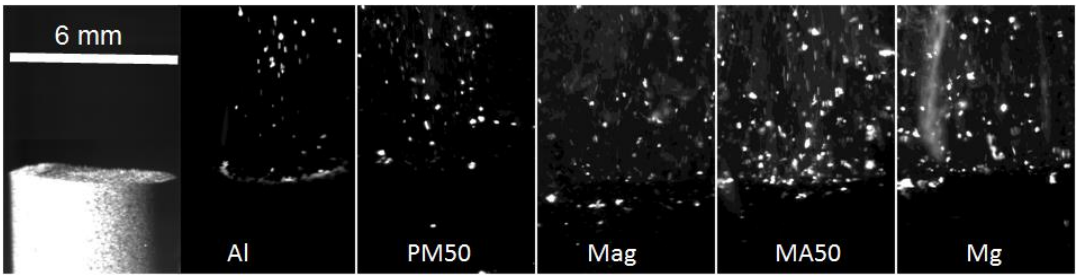

Fig. 8 Burning surfaces of solid propellant containing different metal fuels (all are 15 wt.%). Pressure is 0.1 MPa and all images were taken with the same exposure setting.

Conversely, the other propellants showed ignition at surface with bright combusting particles, especially for neat Mg, MA and magnalium particles. This is due to the lower oxidation onset temperature of Mg that aids the ignition and combustion of Al. The combustion behavior of particles in the gas flow after ignition was different for magnalium and MA particle containing propellants. For the magnalium case, shattering

microexplosion of particles was observed (snapshots of microexplosion is shown in Fig. 9), where particles underwent significant fragmentation, forming a bright cloud of fine particles that rapidly react. In case of MA powder, particle shattering was observed, but the break-up was more modest with few resulting particles. Therefore, mechanism of particle shattering is different for the two cases. No such behavior was observed in neat Al, PM or neat Mg.

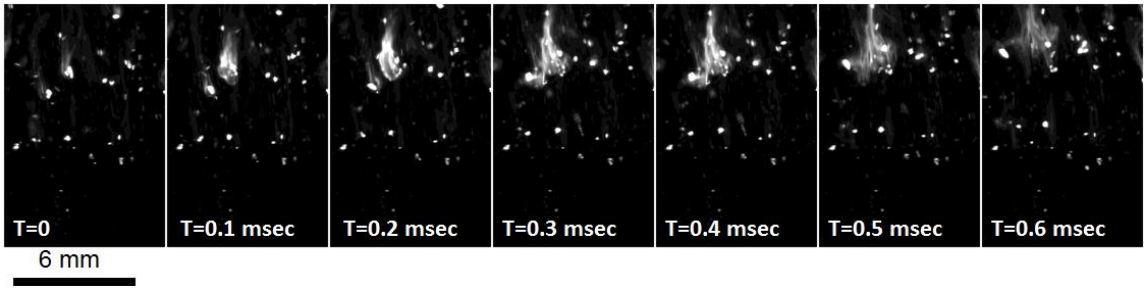

Fig. 9 Image sequence of the burning particles for propellant pellet contains magnalium as additive. Showing the particle shattering far from surface.

Quantitative analysis of agglomeration that result from metal particle inclusion is done using image processing of the collected quench disks. The accuracy of this method depends on the investigated particle sizes. This study is concerned with the agglomerates larger than 10 μm and the error is estimated to be less than 1.63 % [20].

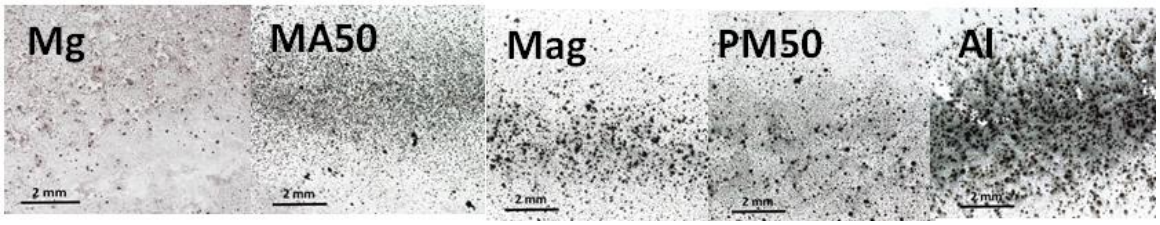

Fig.10 Image for quench disks collected from propellant pellets having metal particle sizes between 25-75 μm, and burning at 6.9 MPa in Argon environment.

The results from quench disk analysis for propellants that have different initial metal sizes (D<25 μm and 25<D<75 μm), burning at two different pressures (1.38 and 6.9 MPa) and different inert gas (N2 or Ar) are reported in Fig. 11 and Fig. 12.

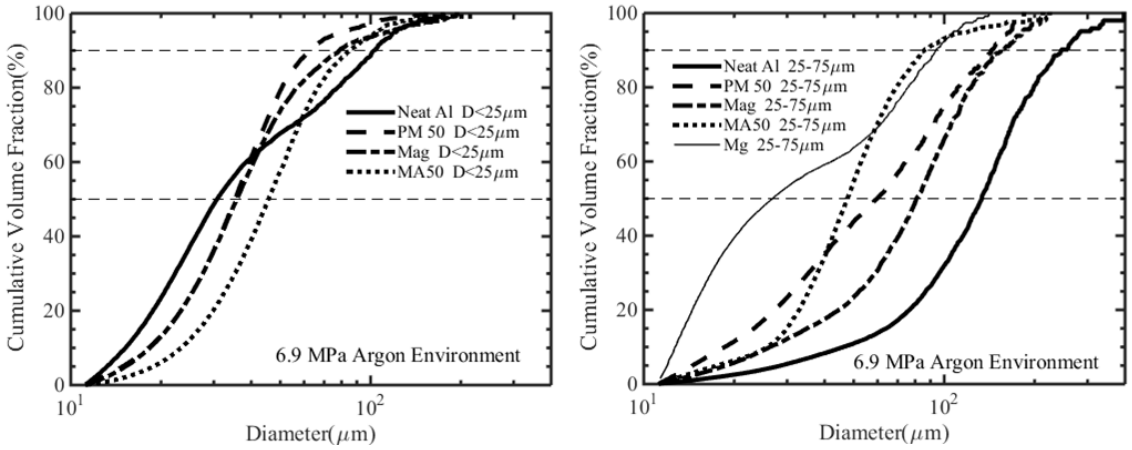

Fig.11 Cumulative volume fraction of products from quench disks from propellants burning at 6.9 MPa in Argon environment with metal additives with particle sizes (a) less 25 μm and (b) between 25-75 μm.

The comparison of agglomeration sizes for initial particle size less than 25 μm shows that physical mixture of spherical aluminum and spherical magnesium results in the smallest agglomeration size, while for initial particle size between 25-75 μm, the neat magnesium and MA powders give lower agglomeration size. This can be explained by considering two factors. First factor is the particle morphology. It has been shown previously [18] that flake Al has agglomeration tendency larger than spherical Al although it has lower ignition temperature [21]. This factor dominates in the small initial particle size range for the MA particles that have a similar flake like morphology. The second factor is the "Particle shattering "and/or "Microexplosion", depending on the homogeneity of particle. From the SEM images of MA powder, the particles in small size range are seen to be more homogenous with a good distribution of aluminum and magnesium. However, this is not the case for the larger particle sizes. There are large separate regions of aluminum and magnesium, which increase the probability of particle break-up when ignited in solid propellant environment. These factors result in similar product size distributions for MA particles less than 25 μm and in the range 25-75 μm.

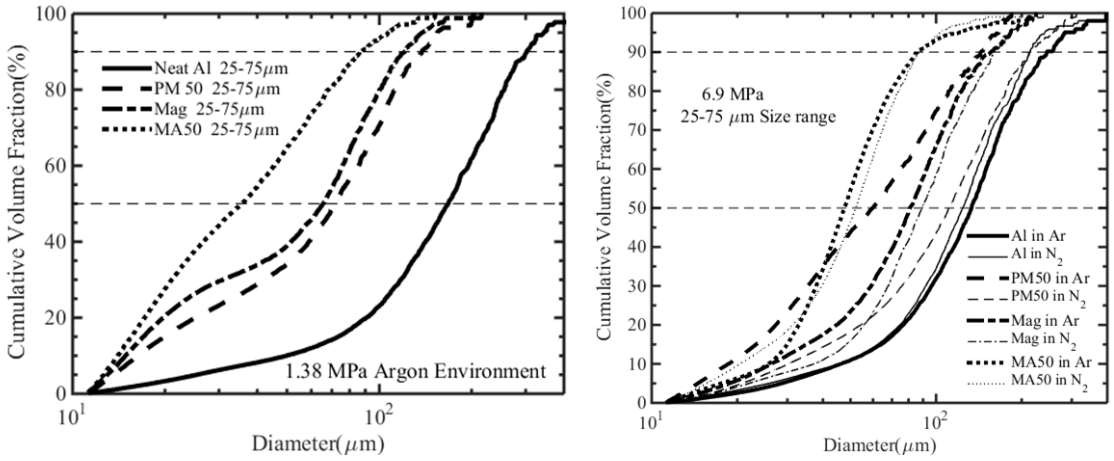

Fig.12 Cumulative volume fraction for quench disks left: Propellant having additive with particle size between 25-75 µm and burning at 1.38 MPa, right Propellant having additive with particle between 25-75 µm, all are burning at 6.9 MPa in Argon/Nitrogen environment.

However, the mechanism is different in case of magnalium, which is an alloy with a homogenous elemental distribution. Magnalium has tendency to microexplode depending on ambient pressure.

The microexplosion phenomena consists of two stage; first stage is "Bubble Generation" in which a bubble is generated due to thermal fluctuations and intermolecular interaction. This bubble generation may be either homogenous which requires a higher superheat limit or heterogeneous where there is dissolved gas or impurity which can act as nucleation site. The second stage is "Bubble Growth", where the bubble formed in the first stage continue to grow, where this growth is governed by Rayleigh-Plesset equation [12],

$$\frac{P_B(t) - P_\infty(t)}{\rho_L} = R\frac{d^2R}{dt^2} + \frac{3}{2}\left(\frac{dR}{dt}\right)^2 + \frac{4\nu_L}{R}\frac{dR}{dt} + \frac{2S}{\rho_L R}$$

where P_B is the pressure within the bubble, P_∞ is the external pressure away from the bubble, R is the radius of the bubble, ν_L is the kinematic viscosity of the liquid, S is the surface tension, ρ_L is the density of the liquid and t is time. It is clear that a higher external pressure suppresses the bubble growth, increasing the time to reach critical size suitable to cause microexplosion, which might exceed the life time of particle itself. This may explain the difference in magnalium behavior at 1.38 MPa and 6.9 MPa in comparison of behavior

of physical mixture. At the relatively lower pressure of 1.38 MPa, there is some probability of microexplosion that can result in lower agglomeration size compared to physical mixture case while at 6.9 MPa, the pressure is too high that it suppresses any bubble growth, resulting in agglomeration size larger than physical mixture case.

The ambient environment may have effects in some cases. For example, running the particle capturing experiments in nitrogen rather than argon showed difference only in case of physical mixture of Al and Mg, the difference in all other cases are insignificant. This is due to the formation of magnesium nitride (Mg_3N_2) from the free Mg particles. This phase is yellowish green in color and its formation has been observed both on the inside of the combustion vessel as well as on the surface of the quench disks used for particle capturing.

2.4 Conclusions

This study shows that mechanical activation of Al-Mg decreases the ignition time of the particles, and their inclusion in propellants results in reduced agglomeration size compared to the physical mixture of the neat metals through lower residence times on the propellant surface and particle shattering in the gas flow. However, propellants with neat Mg had the smallest agglomerates due to their rapid oxidation tendency. The initial MA particle size had little effect on the product sizes, so larger particles can be used for propellant formulations with better mixing characteristics. The MA particles were observed to deviate from the overall composition (50 % Mg) significantly depending on the particle size. Particles less than 25 μm had compositions about 35 % Mg, whereas larger particles in the range 25-75 μm had an average composition around 60 % Mg. The magnalium alloy particles that had the same composition had favorable ignition and combustion characteristics compared to neat Al and exhibited microexplosion phenomena that resulted in smaller agglomerate sizes as well at lower pressures. However, large combustion pressures tend to suppress this and no product particle size reduction due to this effect was observed at a pressure of 6.9 MP

CHAPTER 3. ON THE EFFECT OF MAGNESIUM CONTENT ON THE PERFORMANCE OF ALUMINIZED COMPOSITE SOLID PROPELLANT

3.1 Introduction

Magnesium (Mg) has been studied extensively as an ingredient in solid propellants and pyrotechnics with most of the work focusing on ignitor and flare applications [22]. Mg used in ammonium perchlorate (AP) hydroxyl-terminated polybutadiene (HTPB) propellants increases the burning rate due to increased condensed phase heat release. [23]. The search for environmentally friendly propellants initiated interest on ammonium nitrate (AN) to replace AP as the oxidizer. However, AN propellants have lower burn rates and do not burn aluminum (Al) efficiently. Mg has been studied in these aluminized AN propellants to examine its effect on agglomeration and Al combustion efficiency [24]. The results showed that Mg did not significantly reduce the tendency of Al to agglomerate and therefore had no effect on Al combustion efficiency. However, it was noted that it increased the burning rate of the propellant due to increased heat feedback to the propellant surface [24].

Neat Al and Al 90%/Mg 10% alloy propellants were studied in order to understand the effect of metal properties on burning rate and agglomeration size. The results show that effect of metal on either burning rate or agglomeration size depend to large extent on amount of metal in propellant. As for 10% metal only, aluminum additive results in better burning rate and lower agglomeration size, but this trend is reversed at higher metal loading of 20% and 30% [28].

Previous studies on ignition and combustion of Al/Mg alloy particles were performed at high temperatures and pressures in oxygen [25], water vapor and argon [26]. The particles were ignited using reflected shock in a single pulse shock tube. The results showed

that the contribution of heterogeneous reactions to the heating of the particle is found to besignificant at lower temperatures, but could be neglected at gas temperatures above 3000 K. In addition, as little as 10 wt.% Mg reduces the ignition delay time substantially at all pressures tested. The particle ignition delay times decrease with increasing Mg content, but this reduction becomes less pronounced as oxidizer temperature and pressure are increased [25]. Al/Mg alloy particles have also been shown to enhance the decomposition reaction of AP. It was found that either a mixture of Al and Mg or as an alloy, AP/Al/Mg shows a reduction in the decomposition temperature as well as increase in heat of reaction [27].

For applications requiring very short ignition delay and very short burning time, e.g. ramjet applications and high pressure solid propellants, it is desirable to complete particle burning within approximately 10 ms. This can possibly be achieved by suitably alloying Al with Mg. However, Al-Mg alloys containing more than about 1 at. % Mg are two-phase alloys. (The room temperature solid solubility of Mg in Al under equilibrium conditions is less than 1 at.%). Working with a single-phase material is desirable to understand the combustion behavior of particles. Mechanical activation may increase this solubility limit up to 40 wt.% Mg [29]. Mechanically activated (MA) Al/Mg particles have been synthesized and used as hydrogen generation materials when mixed with ammonia borane and water [30]. Aerosol combustion in air with MA powders showed higher rate of pressure rise and shorter ignition delay compared to pure Al, where the MA particles show two stage burning mechanism, with the first stage gradually disappearing with increased Al concentration [31]. MA Al/Mg powders investigated in hydrocarbon flames showed that an increase in Mg concentration led to longer burn times for the alloy particles for all flame conditions. For all compositions, alloy particles burned longer than similarly sized Al particles except for the alloy with the smallest concentration of Mg [32].

Our previous work [33] showed that MA Al-Mg can reduce the agglomeration sizes of the combustion products. However, it is less energetic compared to pure Al. The objective of this research is to find the minimum amount of Mg that can still have substantial amount of agglomeration size reduction with minimum loss of specific impulse.

3.2 Experimental

Starting materials included 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 MA planetary mill. Nominal powder composition was 50:50 (MA50), 70:30 (MA70), 90:10 (MA90) and 95:5 (MA95) for Al/Mg by weight. The rotational speed was set to 200 rpm. The direction of rotation was set to reverse every 15 min. The same two step milling procedure is applied as discussed elsewhere [33]. The powders are sieved to two particle size ranges (i.e. less than 25 and 25-75 μm ranges).

Morphology of the prepared powders were investigated using FEI Nova 200 Dual Beam Scanning Electron microscope. A Malvern Mastersizer 2000 with Hydro 2000 lP dispersion unit is used to verify the particle size distributions of the sieved MA composite powder. Phase compositions of the powders were analyzed using X-ray Diffraction (XRD) (Bruker D8 Focus diffractometer) with 5 deg/min scan rate.

Coherent GEM 100A CO2 laser beam is used in determining ignition delay times for loose powder ignition setup discussed elsewhere [34]. Propellants consisted of 14 wt.% of a hydroxyl-terminated polybutadiene (HTPB) binder (cured with isophorone diisocyanate IPDI), 71 wt.% AP (80 wt.% coarse 200 μm and 20 wt.% fine 20 μm, ATK), and 15 wt.% of sieved composite powders. The ignition of metal particles at the propellant burning surface was observed at 1 atm pressure using a high speed video camera (Vision Research, Phantom v7.3) at 10,000 frames/s (fps). Propellant agglomerate products were collected using the device discussed elsewhere [35].

3.3 Results and discussion

Particle Morphology and size:

Figure 1 shows SEM images of the MA powders. All the powders had the same flake morphology and similar dimensions.

The particle size distributions for all prepared powders are shown in Fig. 2. The size distributions of sieved powders are almost identical for both the size ranges investigated.

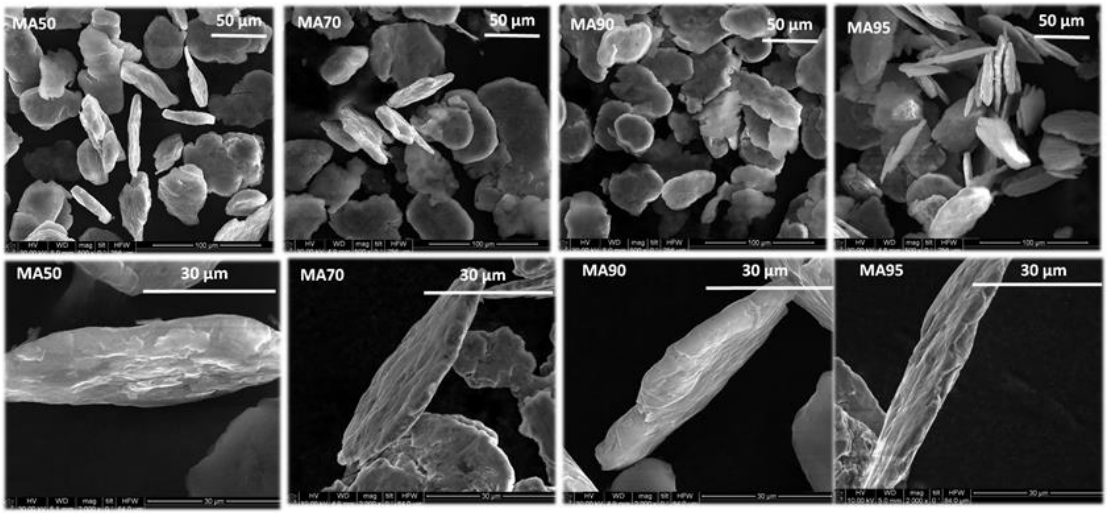

Fig. 1 SEM images of MA50, MA70, MA90 and MA95

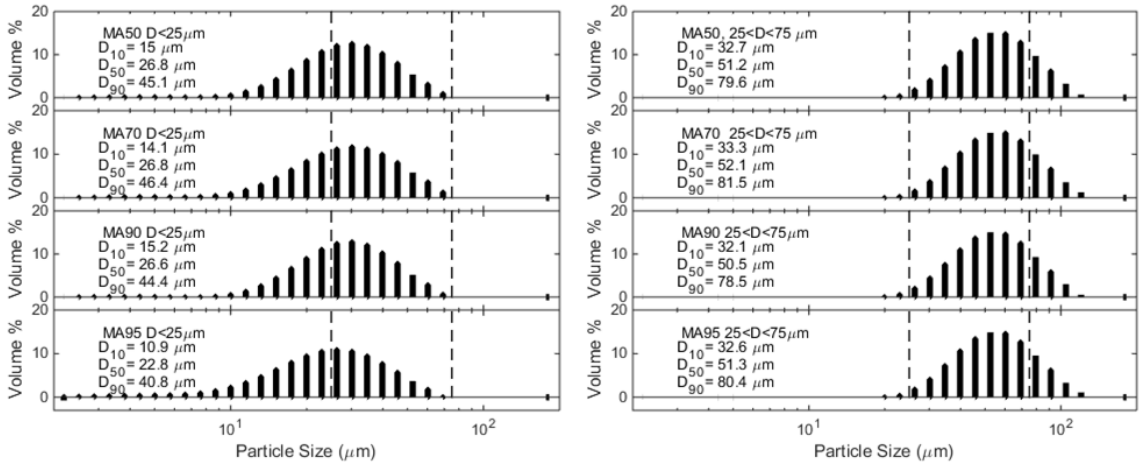

Fig. 2 Particle size distribution for sieved prepared powder for small size range (left) and large size range (right)

Phase Composition (XRD)

Structure and composition of the powders were characterized by x-ray diffraction (XRD) and are shown in Fig. 3. For the MA powder, the pattern shows only peaks of Al and Mg are present, with vanishing Mg peaks at lower concentrations. No peaks for any other phase were discernable, indicating there was little to no reaction during the MA process.

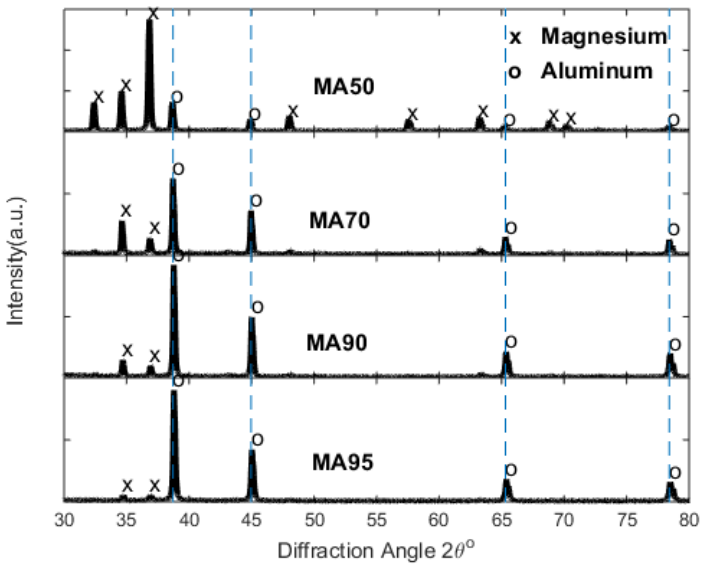

Fig. 3 XRD patterns of MA powders.

Thermochemical Calculations

Metal addition affects several propellant properties that can influence the burning rate. It can also change the propellant stoichiometry and, thus, burning rate, depending on what ingredients the metal replaces in the formulation. Thermochemical equilibrium calculations were performed on AP/HTPB propellant formulations containing Al/Mg using the Cheetah 6.0 equilibrium code to determine the effect of the amount of Mg on condensed phase products ,flame temperature and specific impulse [36]. This was accomplished by replacing aluminum with Mg in a propellant containing 71 wt.% ammonium perchlorate (AP), 14 wt.% hydroxyl terminated polybutadiene (HTPB), and 15 wt.% of either aluminum or Al/Mg composite. A chamber pressure of 6.9 MPa and ideal expansion to equilibrium products at 0.1 MPa was assumed. The results for these calculation are shown in Fig. 4 and Fig.5.

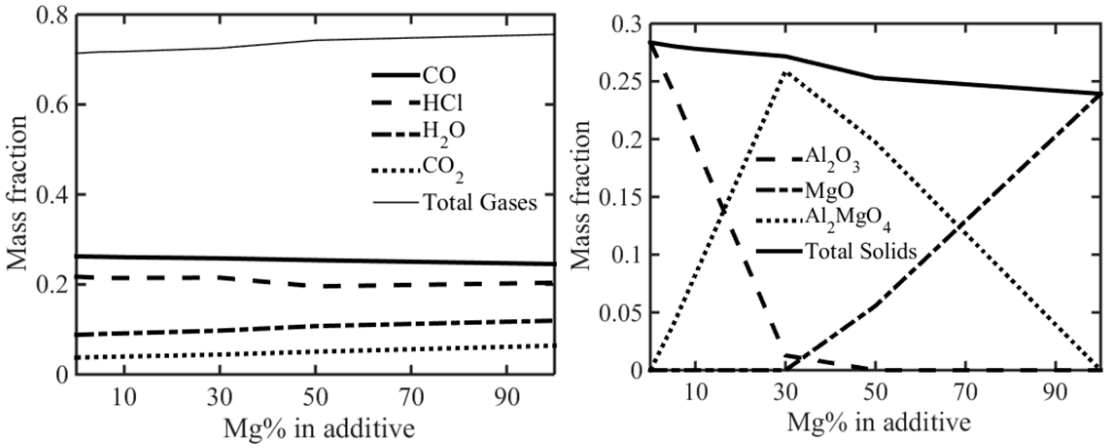

Fig. 4 Mass fraction of gaseous products (left) and condensed phase products (right) for a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either aluminum or Al/Mg composite

From Fig.4, it can be seen that alumina in condensed phase products is replaced by magnesia for Mg percentages higher than 30%. The total mass fraction of condensed phase decreases as Mg percentage increases. Figure 5 shows that, the specific impulse which is the main performance index for solid propellants keep decreasing with increasing Mg percentage, with a loss of 5 seconds at 100% Mg.

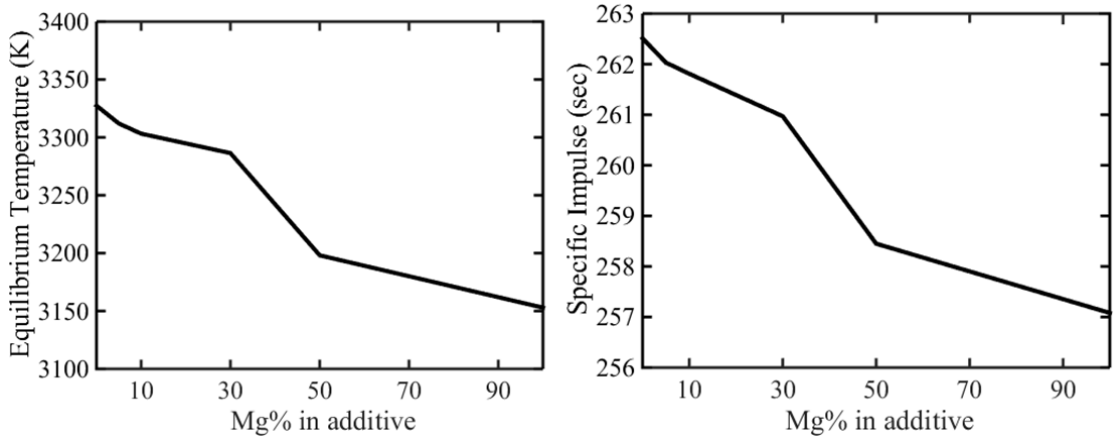

Fig. 5 Effects of the amount of Mg in 15% additive for a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either aluminum or Al/Mg composite

However, the oxidation state of Al (Al oxidizes to Al2O3) differs from magnesium (Mg oxidizes to MgO) and replacing Al with Mg will shift the oxidizer to fuel ratio for the propellant. As a result, optimization is needed to find the formulation that gives the highest

specific impulse for each Mg percentage. The results of these detailed calculations are shown in contour plots and summarized in Table 1.

Table 1. Summary for optimum formulation for AP/HTPB propellant

Mg% in additive	Max Isp (sec)	Chamber Temp.(K)	Solids Loading	Al	Mg	AP	HTPB
100	259.58	3166.03	87	0.00	23	64	13
50	259.87	3312.92	86.71	10.12	10.12	66.47	13.29
30	262.79	3424.45	86.68	14.5	6.22	65.96	13.32
10	263.74	3539.00	88	19.36	2.15	66.48	12.01
0	264.78	3614.89	89	22	0.00	67	11

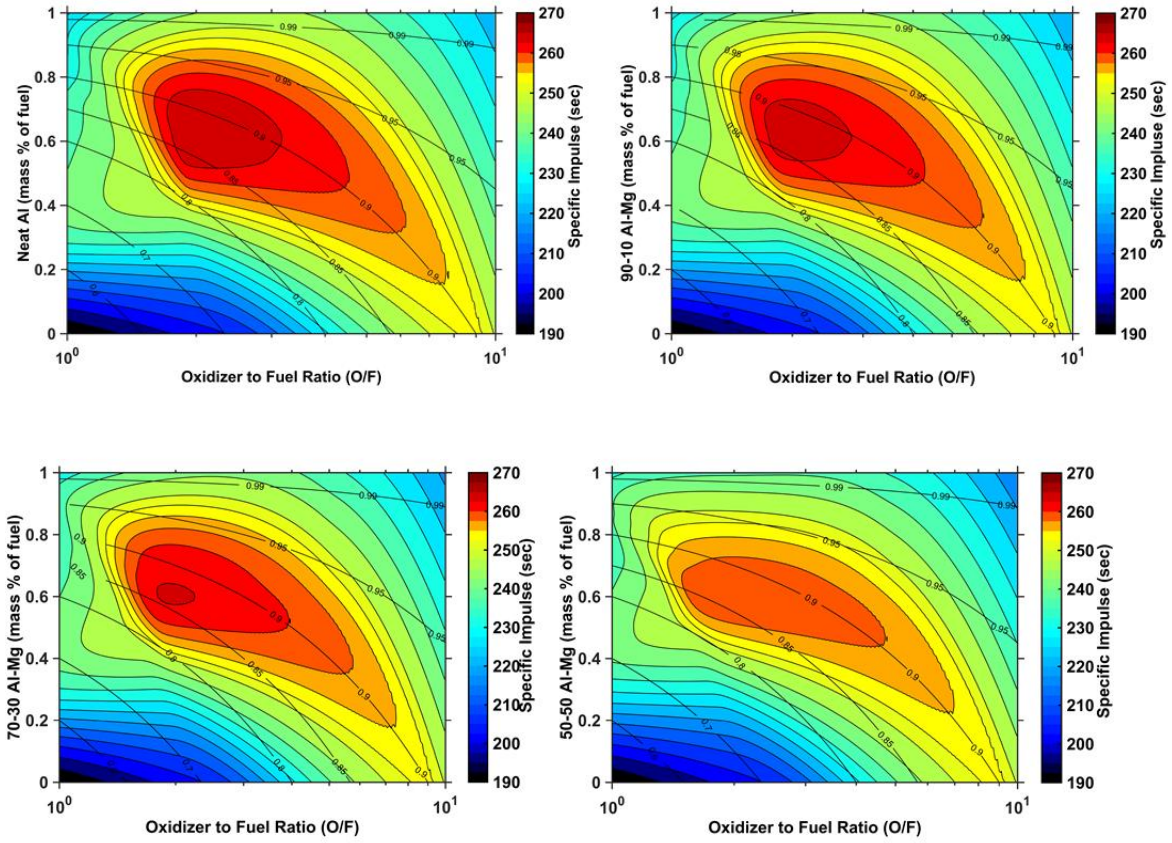

Fig. 6 Effects of Mg percent on optimum formulation

The results for these optimum formulations reveal that addition of Mg decreases specific impulse. For neat aluminized propellant, solids loading can be increased to 89%

rather the used one of 86%. However, for better rheology [37], the 86% solid loading was used for experiments. This is also close to the optimum solids loading for pure Mg (87%).

Loose Powder Ignition

Coherent GEM 100A CO2 laser beam is used in determining ignition delay times for loose powder ignition setup discussed elsewhere [34]. Fig.7 shows the ignition delay for all prepared composite particles, for both size ranges.

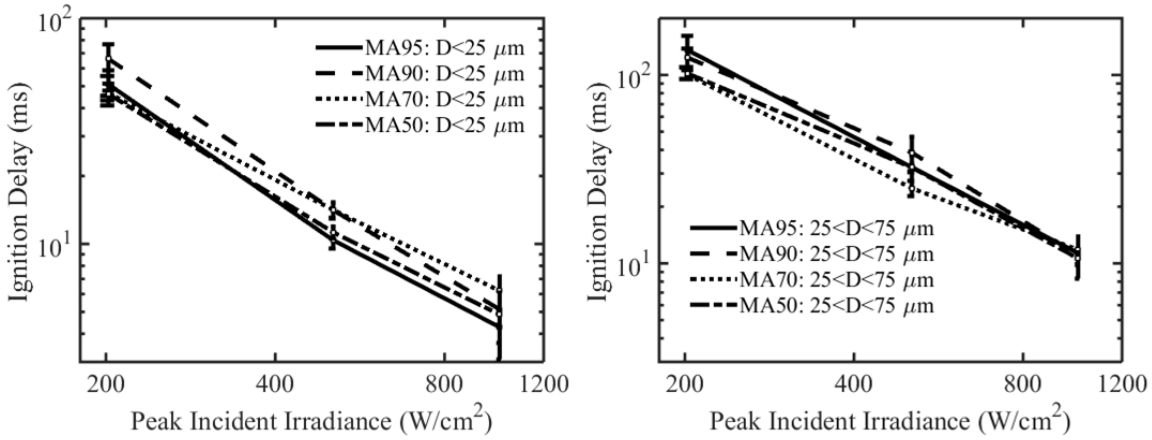

Fig. 7 Ignition delay times for MA powders with diameter less than 25 µm (left) and powders sieved between 25-75 µm (right).

The results show no statistically significant difference between ignition delay times for particles with any Mg content and the variations between ignition delays are within experimental uncertainty. However, videos from ignition experiments showed that the brightness of ignited particles are lower with lower magnesium concentration. This is in agreement with the previously proposed two stage burning mechanism [31], where, an initial Mg-dominated combustion event is followed by combustion of the remaining Mg depleted Al. The Mg-dominated burning stage gradually disappears with increasing Al concentrations.

Propellants

Propellant Burning rates

The burning rates for solid propellants containing 15% additives were investigated at pressure. The 15% additive was either a PM of Al and Mg, or MA powder with the same weight ratios (i.e. 50:50, 70:30, and 90:10). All the propellants investigated showed plateau

burning regime (the burning rate curve deviate from the typical power relation between pressure and burning rate namely St. Roberts Law) starting at around 6.9 MPa but some had the plateau region extend to 13 MPa. Previous studies on plateau burning showed that propellants with coarse to fine oxidizer ratio larger than 60:40 (in propellant use, it is 4) has higher chance of producing a plateau burning regime [38].

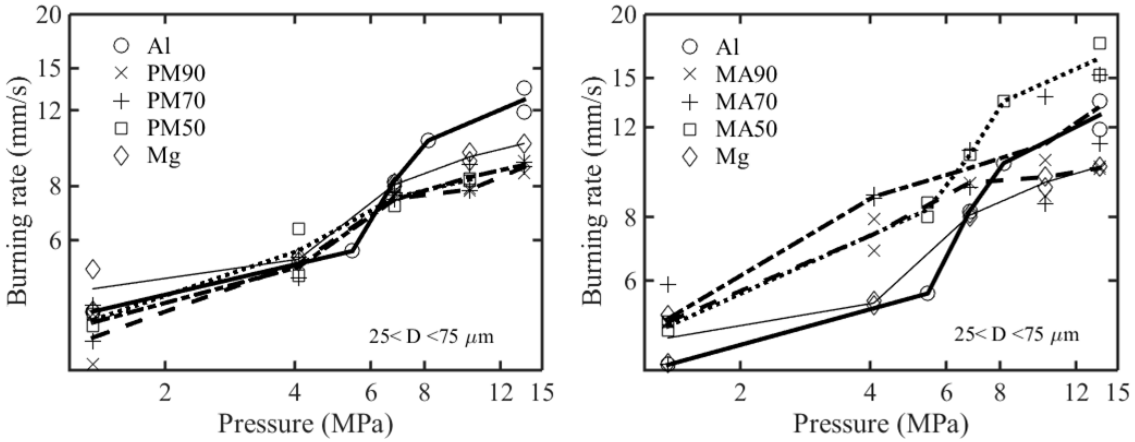

Fig. 8 Burning rates for solid propellant with Mg inclusion, Left: physical mixture of Al/Mg. Right MA Al/Mg composite powder both in a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

As might be expected, the Mg inclusion increased burning rates as Mg is easily ignited. This produces larger condensed phase heat release, which increases heating of the surface layers of solid propellant. However, the effect of adding Mg differed between PM and MA cases.

Fig.9 shows that for PM, increasing Mg percentage slightly lowers the burning rate, which may be attributed to lower flame temperature (from 3320 K for 100% Al to 3150 K at 100% Mg) that counteract the effect of Mg reactions at surface (Fig. 10). However, this behavior is reversed in case of MA powder, where increasing Mg percentage increase burning rate about 50 % at 6.9 MPa. This behavior may be explained by the fact the MA particles (which contain both Mg and Al) rapidly ignite at the propellant surface (Fig. 11), so the heat feedback to the surface due to increased condensed phase heat release is increased, and is larger than in case of PM.

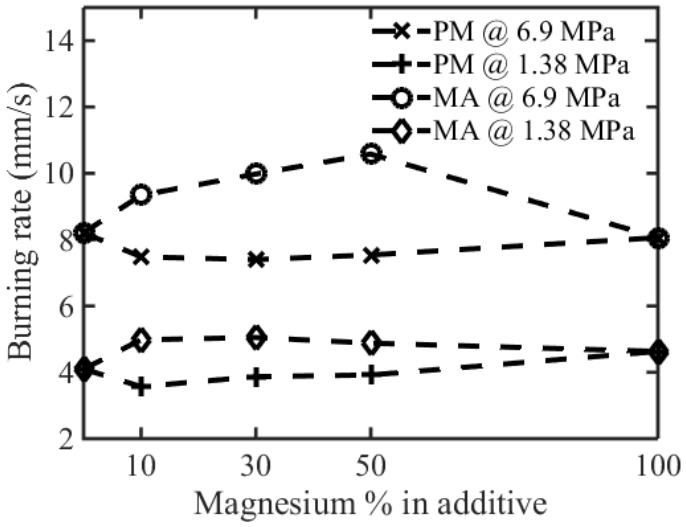

Fig. 9 Burning rates for solid propellant as function of Mg inclusion, a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

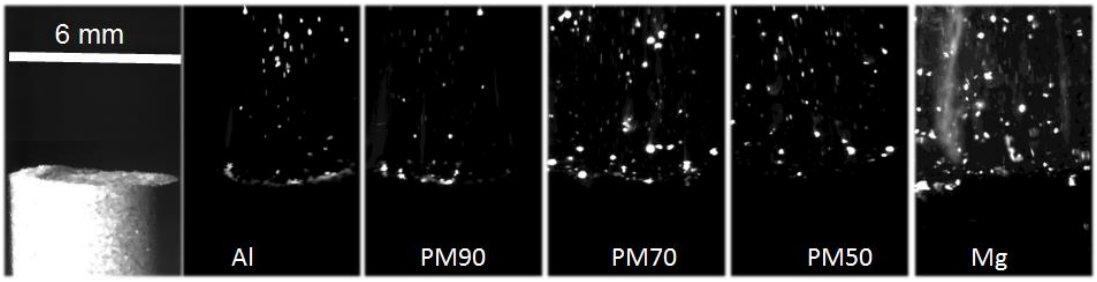

Fig. 10 Solid propellant pellet (left) and burning surfaces of pellets containing sieved spherical Al, PM90, PM70, PM50 and Neat Mg. Pressure 0.1 MPa and all photos were taken with the same exposure settings.

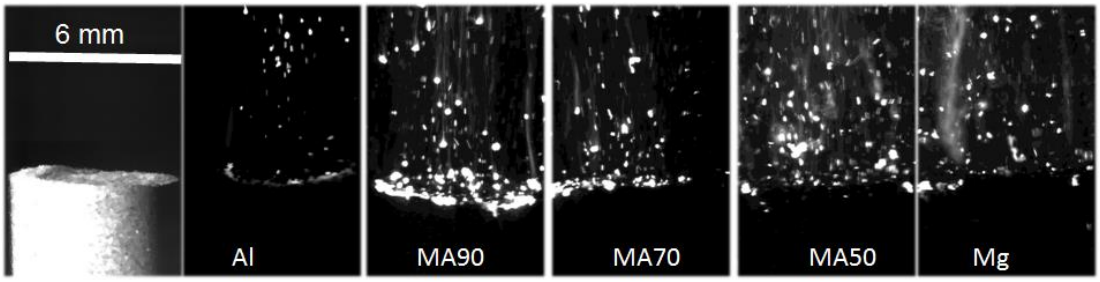

Fig. 11 Solid propellant pellet (left) and burning surfaces of pellets containing sieved spherical Al, MA90, MA70, MA50 and Neat Mg. Pressure 0.1 MPa and all photos were taken with the same exposure settings.

Particle Capture

Fig. 12 and Fig. 13 show the collected quench disks for neat Al and both PM and MA powders for propellants containing metal additives with particle sizes between 25-75 µm. The images show qualitative differences between MA and PM at different Mg amounts, especially for MA50 and MA70. For both PM and MA additives, the particle sizes increase as the amount of Al is increased due to agglomeration of the particles at the surface of the propellant. However, the MA quench disks show that the particles are finer than those in PM.

Fig. 12 Burning rates for solid propellant as function of magnesium inclusion, a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

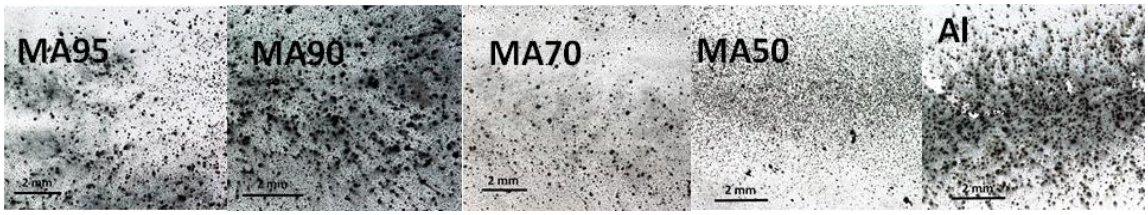

Fig. 13 Burning rates for solid propellant as function of Mg inclusion, a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

Fig 14. shows the cumulative volume fraction for propellants using PM of spherical Al and spherical Mg. The trends are similar for both particle size ranges, where increasing Mg percentage lowers the cumulative volume fraction compared to neat Al. Fig. 15 shows the quantitative analysis for the propellants using MA powders. Here, the trends were different for the two particle size ranges. For the large particle sizes, the trend is similar to PM case, where increasing Mg percent results in lower agglomeration sizes with respect to neat Al.

However, the trend is reversed for the small particle sizes, the MA powders result in larger agglomeration sizes than neat Al.

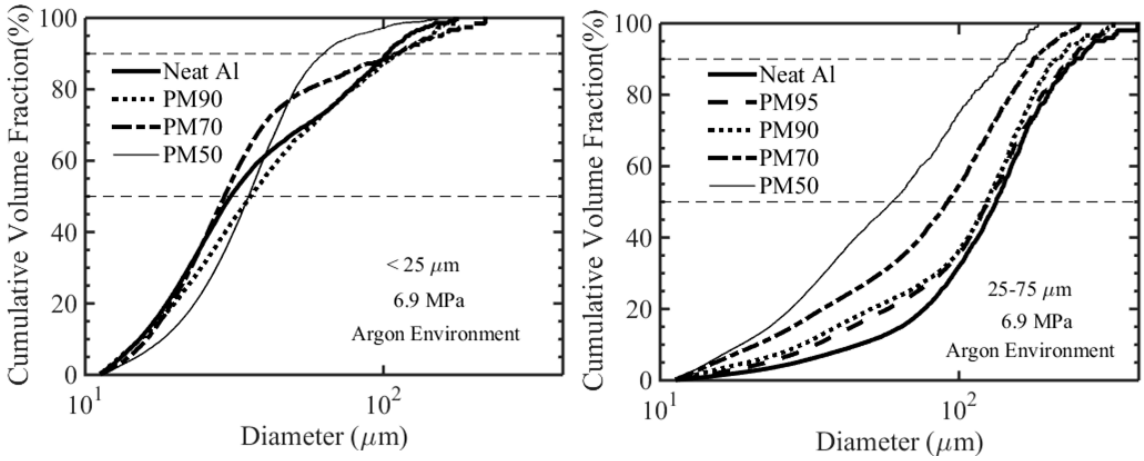

Fig. 14 Burning rates for solid propellant as function of Mg, a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

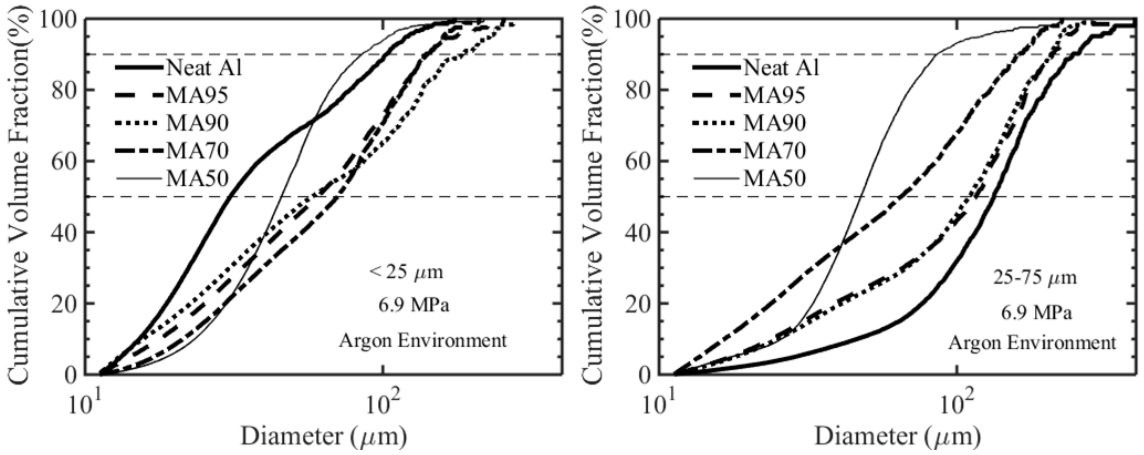

Fig. 15 Burning rates for solid propellant as function of magnesium inclusion, a propellant containing 71 wt.% AP, 14 wt.% HTPB, and 15 wt.% of either PM or MA Al/Mg powders

The trends in cumulative volume fraction can be explained by combining two factors, particle morphology, and particle tendency of break-up or shatter. All MA powders are flake shaped, and they have a large tendency to agglomerate. However, for the large particle size range, it has been shown previously that the particles have heterogeneous internal structure [33], which increase the tendency of particle shattering. For the small particle size, the particles internal structure is more homogenous, so the tendency to shatter

is less, leaving only the particle morphology effect in play. Quantitative analysis results for collected quench disks for propellants containing larger particle size range are summarized in Table 2. In general, propellants containing PM and MA particles have lower agglomeration sizes than the neat Al propellants. Comparison between MA and PM for the same Mg percent shows that MA propellants are always better than PM propellants.

Table 2. Relative reduction of representative diameters from neat Al to PM/MA

	Al	PM95	PM90	PM70	PM50	MA95	MA90	MA70	MA50
D_{10}	46	-31	-36	-44	-53	-48	-46	-61	-46
D_{50}	133	-4	-7	-26	-50	-14	-17	-63	-65
D_{90}	245	-4	-11	-26	-40	-15	-16	-50	-65

Table 3. Relative reduction of representative diameters from PM to MA at different Mg %

	5% Mg	10% Mg	30%Mg	50% Mg
D_{10}	-27	-17	-14	39
D_{50}	-9	-11	-47	-22
D_{90}	-10	-3	-31	-41

3.4 Conclusions

In this work, the two step milling procedure for MA Al/Mg particles was extended to Al-rich region up to 95% Al. MA particles at different Mg contents had similar flake like morphology and particle size distributions. Ignition delay experiments using a CO2 laser showed no effect of Mg percent on ignition delay, while lower Mg contents result in “less bright” combusting particles. This is due to the lower ignition temperature of Mg enhancing the combustion of composite particles.

For the small particle size range (D <25 μm), flake like morphology of the MA particle containing propellants produce larger agglomerates compared to the PM. This was explained by the absence of shattering mechanism due to uniform mixture of the components within particles, hence the particle morphology is the dominant factor.

However, for the size range 25-75 μm particles, shattering due to inhomogeneity in internal particle structure, is more dominant.

Effects of Mg content on burning rate of aluminized solid propellants depend on whether Mg is physically mixed at a coarse particle size level or intimately mixed using MA. For MA, increase in Mg percentage results in increase in burning rate up to 50 wt.% Mg. However, the behavior is reversed in case of PM. In MA case, the whole particle ignites at propellant surface, which increases the amount of heat release in condensed phase and provides higher feedback to the propellant surface. In PM, the higher amount of ignited Mg particles with lower flame temperatures decrease heat feedback, which counteracts the increased heat release rates in condensed phase.

There is a compromise between loss of specific impulse due to reduced heat of oxidation and gain in specific impulse due to lower two-phase losses with reduced agglomerate size with increasing Mg content. MA70 may be suggested as the optimum composition, which has a loss in specific impulse (-2 sec), but with possibly higher gains due to the reduction in agglomeration size (30% compared to 40%) that can reduce two phase flow losses.

CHAPTER 4. EFFECTS OF MECHANICAL ACTIVATION PARAMETERS ON MAGNALIUM BEHAVIOR IN ALUMINIZED COMPOSITE SOLID PROPELLANTS

4.1 Introduction

Magnalium has been known since 1908 [39]. It combines good characteristic from magnesium and aluminum as it has low ignition temperature as magnesium with high density and high energy content as aluminum, also it is easily grounded into fine powders because of its brittleness or atomized, it also allows using large particle size because of it is easily ignited, which reduce fire hazard and cost [40]. Magnalium also has been used in enhancing ignition for Boron based propellant in ramjet [41,42].

AN based propellant has such problems as much lower burning rate and higher pressure deflagration limit (PDL) comparing with the conventional AP based propellant. Magnalium (Mg-Al) which is the alloy of Mg and Al was added to AN based propellant as a metallic fuel and found to be effective to improve the combustion characteristics. Burning rate increases along with the amount of Mg-Al, and PDL decreased. [43]. Magnalium also was used as metal additive in modified double base propellant, it results in significant change in pressure sensitivity, and larger aggregation/agglomeration phenomena in combustion products than that of the blank propellant [44] Replacing Al with Al-Mg in CMDB results in burning rate increase, pressure index decreases, with the combustion efficiency of Al decrease [54].

Magnalium was also applied in "*eco-friendly propellant*" where magnesium plays a role in suppressing hydrochloric acid agent in the combustion gases of AP based propellant which results in both high efficiency (99% compared to 94% of aluminized propellant in the same small L* motor) and environment friendly propellant (pH value of

4.5 compared to 2.2 for aluminized propellant [46]. Because magnalium is easily ignited,the temperature gradient near surface was 1.75 time the temperature gradient in comparable aluminized propellant, which results in higher burning rate [47]

Despite of these merits of magnalium. It was verified that, with the same composition and comparable particle sizes metastable MA Al-Mg particles had lower ignition temperature and higher propagation velocities [48], shorter combustion times, and more complete reaction [49] as compared to pure Al, pure powder blends of Mg-Al, or equilibrium intermetallic phases

Ball milling can be classified into two main categories that depend on the starting material used. Ball milling of powders with different compositions, in which material transfer and solid state interdiffusion reaction occurs, is named mechanical alloying (MA) while ball milling of single composition powders, such as single-phase compounds, has been termed mechanical milling (MM). It is significant that ball-milling has been found to induce extensive plastic deformation even into extremely brittle materials [50]. Experiments showed that Partial amorphization of aluminum increasing the system reactivity in Al-Ni systems [51]. It has been shown that crystalline boron has low temperature burning while the amorphous boron has much higher reactivity or explosive combustion [52].

Milled magnalium was shown to have higher burning rate and lower agglomeration size in hydroraective propellant (70% metal), however, they did not show the particle size distribution after milling and also reported the agglomeration at 3 MPa and single value burning rate. [53]

Objective of this research is systematic study of modifications the microstructure of magnalium, which has a single γ -phase. Structure evolution of Mg-Al and combustion characteristics of a solid propellant containing modified Mg-Al alloy are studied

4.2 Experimental

Starting materials included Magnalium (Skylighter -325 mesh), Powders were mechanically milled using a Retsch PM-100 MA planetary mill. Milling balls and jars were

both made of hardened stainless steel. A batch of 35 g of powders in one jar were milled each time with a ball-to-powder ratio of 10:1 in mass and a rotational speed of 200 rpm for low speed milling and 500 rpm for high speed milling. The planetary ball mill was set to continuously run 5 min followed by a break of 15 min, and the rotation direction reversed every 15 min. Active milling time was set to 1 hour. After milling the material was sieved for particle less than 25 microns. Because of brittleness of magnalium, the milling procedure results in breaking all large particles, this results in aggregates of small particles, however longer time sieving will result in all particles pass through the 25-micron sieve.

Powder morphology were investigated using FEI Nova 200 Dual Beam Scanning Electron microscope. The size distributions of the sieved MA composite powder as well as similarly sieved reference powders of as received magnalium were verified using Hirox optical microscope. Phase compositions of the powders were analyzed using X-ray Diffraction (XRD) Bruker D8 Focus diffractometer with 5 deg/min scan rate. Propellant consisted of 14 wt.% of a hydroxyl-terminated polybutadiene (HTPB) binder (cured with isophorone diisocyanate IPDI), 71 wt.% AP (80 wt.% coarse 200 μm and 20 wt.% fine 20 μm, ATK), and 15 wt.% of as received magnalium or MM- magnalium The ignition of metal particles at the propellant burning surface was observed at 1 atm pressure using a high speed video camera (Vision Research, Phantom v7.3) at 10,000 frames/s Propellant agglomerate products were collected using the device discussed elsewhere [54]

4.3 Results and discussion

Figure 1 shows SEM images of the used powders. The first column shows the as received magnalium which is shown to have irregular shape with sharp edges. While the second column show the low speed milled magnalium, it is clear that this low energy milling results in small change in particle morphology as the particle still have the sharp edges shown in as received magnalium. The last column shows the high speed milled magnalium, the low magnification images (the top row) shows that the particle are getting smoother and near spherical shapes, which is in close agreement with [55]

Fig.2 show the particle size distribution for the three powders, the low speed milled and high speed milled magnalium are almost identical, however the sieved as-received

magnalium is larger, However, this difference of particle size cannot be considered order of magnitude difference.

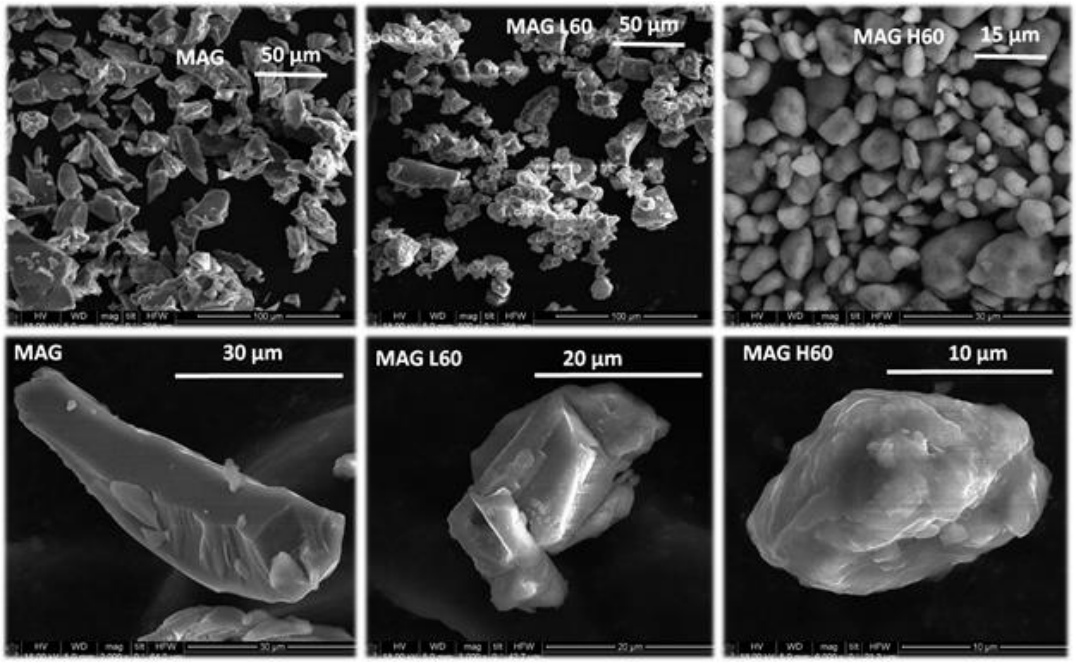

Fig. 1 SEM images of as received Magnalium, low speed milled Magnalium, and High speed milled magnalium

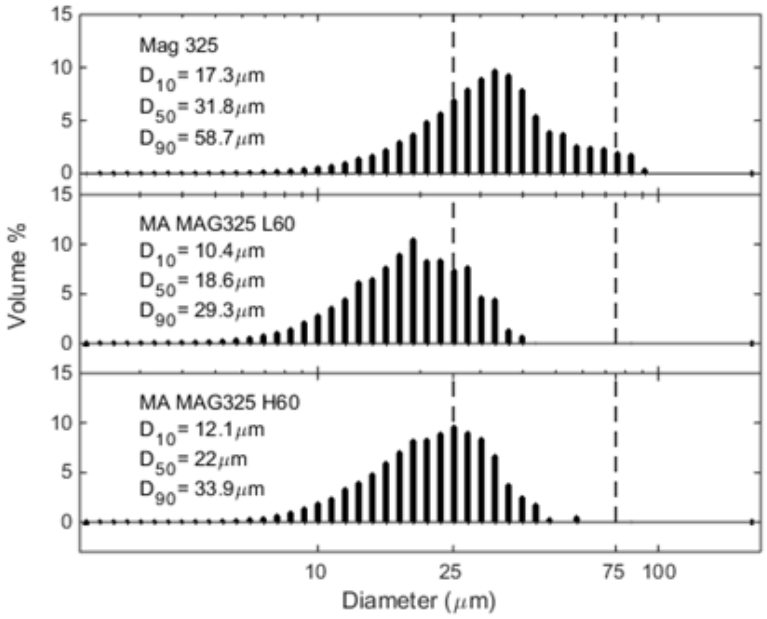

Fig. 2 Particle size distribution for as received magnalium, Low speed milled magnalium and high speed magnalium

The XRD pattern of the as received magnalium, shows sharp diffraction peaks indicating the high crystallinity of the sample. The XRD pattern of the pre-alloyed intermetallic ingot shows (411), (332), (422), (510) and (721) as the intense peaks [56]. While the intensity decreased and width broadened of the characteristic X-ray diffraction peaks for the low speed milling. High speed milling results in noticeable broadening of peaks and decrease in their intensities as a consequence of a strong decrease in crystalline

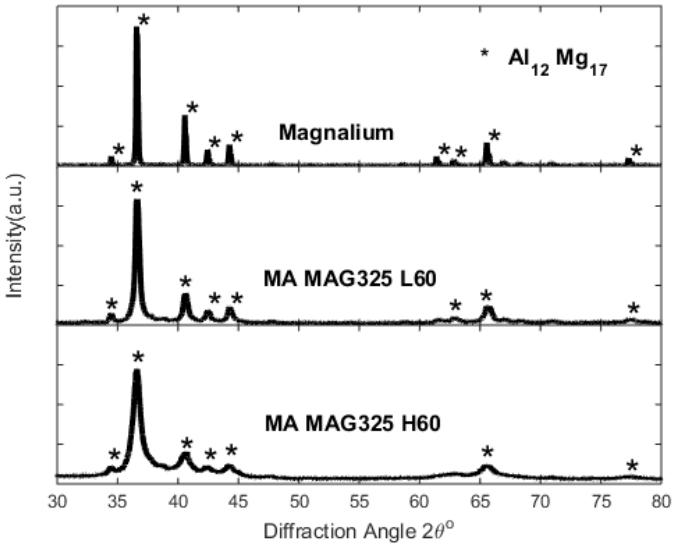

Fig. 4 XRD patterns of as received magnalium, low speed milled and high speed milled magnalium

Linear burning rate for the propellant using spherical aluminum, as received magnalium, low speed milling magnalium and high speed magnalium were evaluated in windowed pressure vessels. The results are compared to MA Al-Mg powder prepared from Al and Mg elements as described elsewhere [57].

The results showed that milled magnalium whether low speed milling or high speed milling has higher burning rate than as received magnalium. However, it is generally less than the MA Al-Mg except at the highest pressure tested. In addition, all magnalium propellant showed less pressure sensitivity than the neat aluminum propellant.

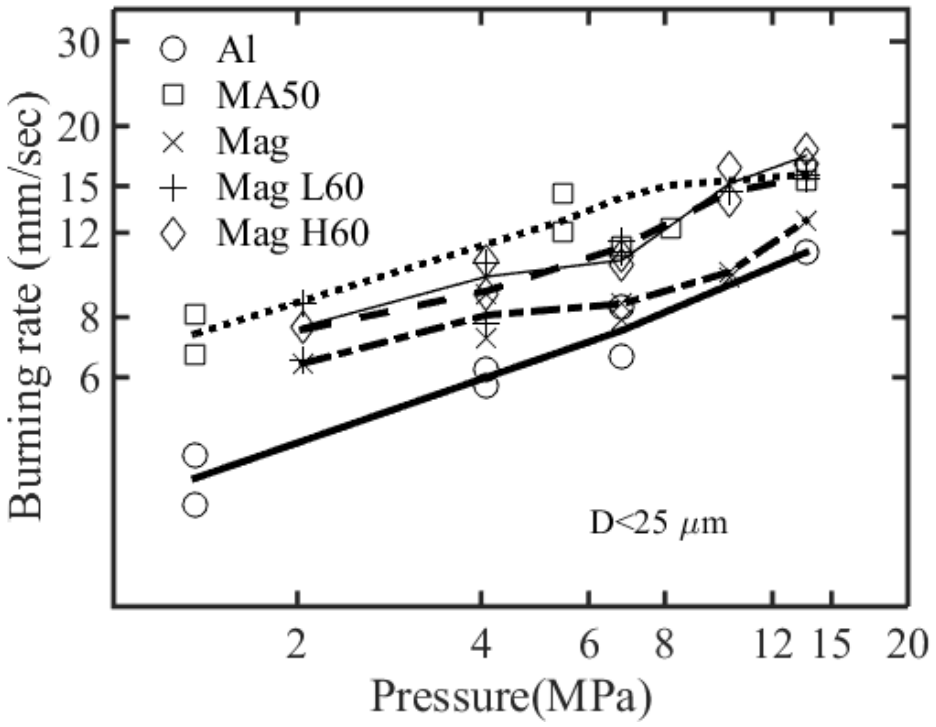

Fig. 4 Burning rate for propellant from 1.36 MPa to 13 MPa.

Analysis of the agglomeration captured using borosilicate disk using a setup discussed elsewhere [54], showed that applying the same milling procedure to both pure elements Al and Mg and as received magnalium results in different burning rate (Fig. 4) and different agglomeration size distribution shown in Fig. 5. Also comparison between as-received magnalium and low speed milling or high speed milling it results that both the high speed milling and low speed milling give better performance.

The enhancement in agglomeration size reduction for milled magnalium whether low speed milled or high speed milled, may be attributed to the small crystallite size and the increase in amorphous phase which results in higher reactivity as shown previously in crystalline and amorphous boron [52].

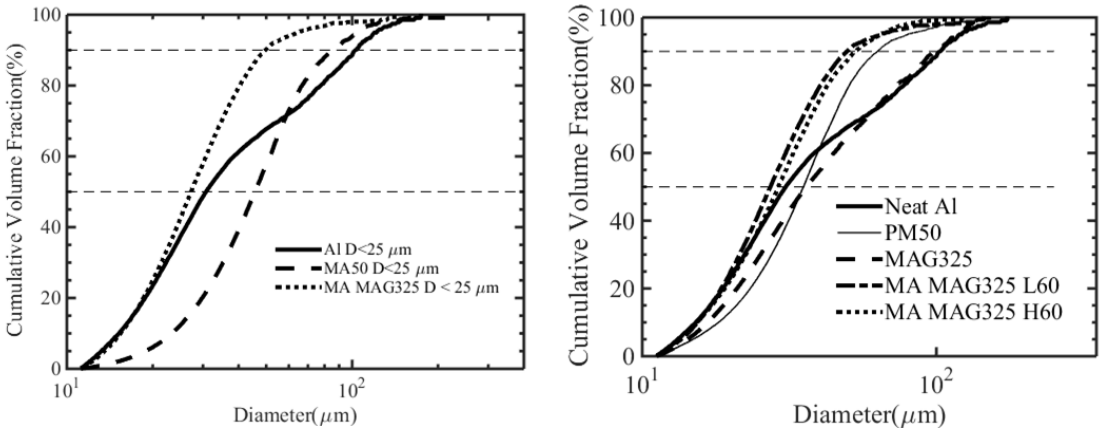

Fig. 4 Cumulative volume fraction for quench disk left: applying same milling procedure to different initial material. Right applying different milling speed to the same initial material.

4.4 Conclusion

Mechanical milling proved to be effective way to increase reactivity of intermetallic as magnalium

Applying the milling procedure to brittle material results in amorphization while when applied to ductile material (elements Al and Mg) does not show any amorphous phase.

High speed ball milling initially brittle material results in crystallite size reduction and decrease of crystalline phase. Which results in higher reactivity. Which in turn results in higher linear burning rate and reduce agglomeration size

CHAPTER 5. PRELIMINARY INVESTIGATION OF THE EFFECTS OF DIFFERENT METAL INCLUSIONS ON ALUMINIZED COMPOSITE SOLID PROPELLANTS

5.1 Introduction

Studies on agglomeration in solid propellants showed that the main cause of agglomeration of aluminum/aluminum oxide particles is due in part to the large temperature disparity between the aluminum melting (660^{o}C) and ignition (~2050^{o}C) temperatures [59]. This disparity results in large residence time of liquid aluminum on propellant surface ending in coalescence prior to ignition. As a results, one remedy for agglomeration problem is to enhance aluminum reactivity in order to reduce residence time at propellant surface.

Mechanical activation (MA) has been shown to be an effective way to altering aluminum reactivity using PTFE [59], Ni [60] or Mg [61]. Previous researches on MA of aluminum with magnesium prevail a new mechanism to reduce agglomeration size i.e. particle shattering. Particle shattering was a result of the internal structure of two metals that have different reaction kinetics namely magnesium which is more reactive than aluminum [61].

Zirconium has been considered attractive additive for solid propellant especially for applications requires high density impulse (zirconium density 6.4 g/cm3 compared to aluminum 2.7 gm/cm3) [62]. It is generally recognized that the zirconium is very ignitable. Its ignition temperature is reduced as the specific surface area increase [63]. This ignitability of zirconium is useful in ramjet application where zirconium particles mixed with the hot air act as ignition source to ensure stable burning [64]

Zr was considered as metal additive in Aluminized composite modified double base (CMDB) propellant using ammonium perchlorate [65] or cyclo trimethylene trinitramine

(RDX) [66], it was shown that optimizing combination of aluminum and zirconium can result in better specific impulse and burning rate compared to neat elements It was found that 25% Zr of total metal additive gives optimum point. [67]. In addition, highly metallized CMDB with Zr as additive showed stable combustion in the range 50-90 bar while corresponding aluminized propellant could not sustain stable combustion [68]

Al-Zr alloy of composition 50:50 has been applied to AP/HTPB propellant., it was found that that the burning rate of propellants containing 35 micron ZrAl alloy particles is higher than that of propellant containing 35 micron Zr particles. Moreover, the burning rate of propellant remained constant regardless of the metal content [10], unlike typical aluminized propellant which reduce burning rate as metal content increase due to increased heat sink effect of metal [69] However Zr containing propellant burning rate show strong dependency on particle size unlike aluminized propellant [70] In addition to its effects on burning rate, it has been shown that two phase losses due to thermal and velocity lag between the condensed phase products and gas in rocket nozzle, is 2.7 times lower than the comparable aluminized propellant , where the decrease in specific impulse due to 1% of Al is 0.22% and 0.078% in Zr. This is because less amount of condensed products and smaller specific heat for these products. [71]

Aluminum has been also alloyed with post-transition metal e.g. Gallium, Powder of Aluminum -5% Gallium showed 200-300 K decrease in ignition temperature compared to pure aluminum with comparable particle size [72]. Alloying aluminum with Europium - which is rare earth metals- was done successfully by the close-coupled gas atomization process. As a result of rapid solidification, the internal structure showed distribution consisted of isolated Al phase and Al4Eu phase which promoted the oxidation of the Al-Eu alloy powder. The DSC/TGA results show that, the oxidation exothermic enthalpy of the Al-Eu powder value is 5 times that of the pure Al powder, in addition the oxidation ratio is twice as that of pure aluminum [73]. Alloy of aluminum and indium phase diagram show an immiscibility gap which is a field in the binary phase diagram which represents equilibrium between two liquids of different composition, by choosing composition between 17.5 % and 96,8 % IN, it is possible to obtain mixtures of indium droplets in an

aluminum-rich host or aluminum-rich droplets in an indium rich host which is possible situation for particle shattering/microexplosion behavior [74].

It has been shown that microexplosion/particle shattering may be a good mechanism to reduce two phase losses in aluminized solid propellant rocket motors by decreasing the agglomeration size [61] . It has been observed that molten zirconium droplet can show fragmentation or explosive burning when burning in environment containing few percent of nitrogen in addition dissolving some impurities in metal prior to ignition produce explosion such nitriding zirconium before burning or dissolving carbon in iron [75]. This behavior of zirconium powder makes it a good candidate for these agglomeration reduction techniques.

The ultimate objective of this research is to discuss the effects that have different metal inclusion having on burning rat and agglomeration size of typical of aluminized composite solid propellant. In this research MA of aluminum with zirconium and indium is performed using high energy ball milling (SPEX 8000). Zirconium and indium was selected as extreme case for differences in melting and /or boiling temperature compared to aluminum. As Indium melt 429.7 K compared to 660 K for Al. where zirconium has boiling temperature of 4650 K compared to aluminum of 2743 K. This difference in melting point is expected to lower melting temperature of the Al-In alloy hence the molten alloy droplets can start reacting earlier than pure aluminum case., while difference in boiling temperature between aluminum and zirconium can induce micro explosive behavior in which the aluminum is the less volatile component.

5.2 . Experimental Methods

Ten-gram batches of Al/In or Al/Zr composite particles were produced from mixtures of either 90% Al aluminum (Alfa-Aesar, 99.8% pure, 325 mesh) and 10% In (RotoMetals 99.99% 325 Mesh) or 10% Zr (Alfa-Aesar, 99.8% 325 mesh) via mechanical activation. 60 mL polypropylene containers (McMaster-Carr 42905T23) using a charge ratio of 12 (73 wt.% 0.95 cm (McMaster-Carr 9529K19), 27 wt.% 0.476 cm (McMaster- Carr 9529K13) 440C steel media) following milling procedures on A SPEX 8000M high energy milling similar to those previously developed [59]. because zirconium is pyrophoric, it is kept

under water, so the powder is dried first in argon filled glove box, then the appropriate amount of powder weighted and mixed with the aluminum inside the glove box. a duty cycle of 1 min ON, 1 min OFF for 30min of total ON time for zirconium and 60 min of total ON for indium. During milling, the container was cooled using a fan. All milled materials were handled in an argon- filled glove box and were dry sieved between 25 and 75 microns and less than 25 microns and their size, morphology, and thermal behavior were determined.

FEI Nova 200 Dual Beam Scanning Electron microscope was used to investigate both powder morphology and elements distribution inside the particles The size distributions of the sieved MA composite powder were verified using Hirox Digital microscope KH-8700 optical Microscope. Bruker D8 Focus diffractometer was used to investigate phase compositions of the powders with 5 deg/min scan rate. a TA Instruments Q600 DSC-TGA was used to investigate the thermal behavior of 1.5–3 mg samples of sieved powders over a temperature range of 100–1000oC. A 20 oC /min heating rate and 100 mL/min flow of a 20/80 vol.% O2/Ar gas mixture were used.

Coherent GEM 100A CO2 laser was used to investigate the reactivity of prepared material in a loose powder ignition setup discussed elsewhere [74]. Propellant formulation of 15% of prepared powder, 71% wt. AP (with bimodal with coarse 200-micron to fine 20-micron ratio 4:1) and 14% of IPDI-HTPB binder was mixed and cured with the same procedure discussed elsewhere [59].

5.3 Results and discussion

Fig. 1 showed SEM images for both elements used in this study and prepared powders, Indium powder is shown to have spherical shape while zirconium powder has irregular shapes with smooth surfaces. For the prepared powder both MA Al90In10 and MA Al90Zr10 has flake shapes with micron and submicron thickness respectively. Particle size distribution of the sieved powder is verified by image processing of high resolution images taken using Hirox KH-8700. From Fig.2 it is shown that the prepared powder is out of range. But this can be explained by the fact that optical sizing or laser sizing consider volume of the particle and find the diameter assuming the particle has spherical shape, so

the sieving results will have a deviation from optical/laser sizing methods, and this deviation increase as the particle shape is far from spherical one,

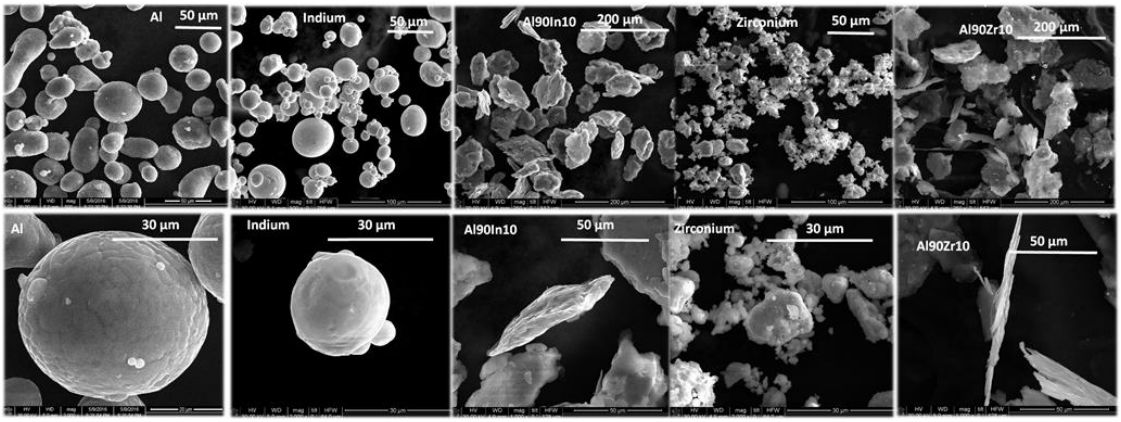

Fig. 1 SEM images of Al, In, MA-Al90In10, Zr and MA-Al90Zr10

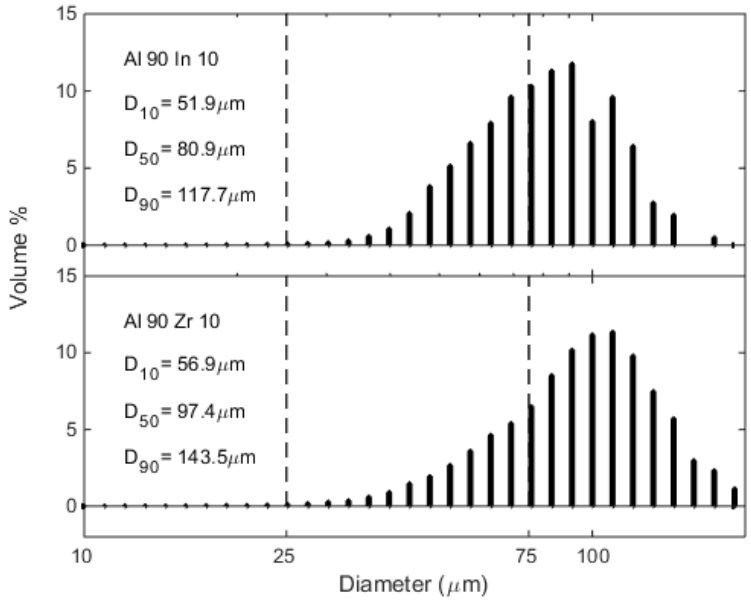

Fig. 2 Particle size distribution for Prepared powder Al90In10, and Al90Zr10

Energy Dispersive Spectroscopy (EDS) maps for the cross sectioned particles (sieved particles between 25-75 microns) are shown in Fig.3. these maps prevail that the although the milling procedure is high energy milling that results in flake shape particles, However, it did not produce a homogenous particle, it was found that the inclusion percentage is different is different from the bulk composition with particle to particle variation. This difference decrease with increasing milling time. For indium the bulk composition is 10%

while the average in investigated particles is only 5% while for zirconium case this average drops to 2.5 % only. This difference can be explained by the fact that mass diffusion in milling procedure is particle size dependent, so it is most probable that the opposite trend will be found for the small size range as verified before in Al-Mg system [61]

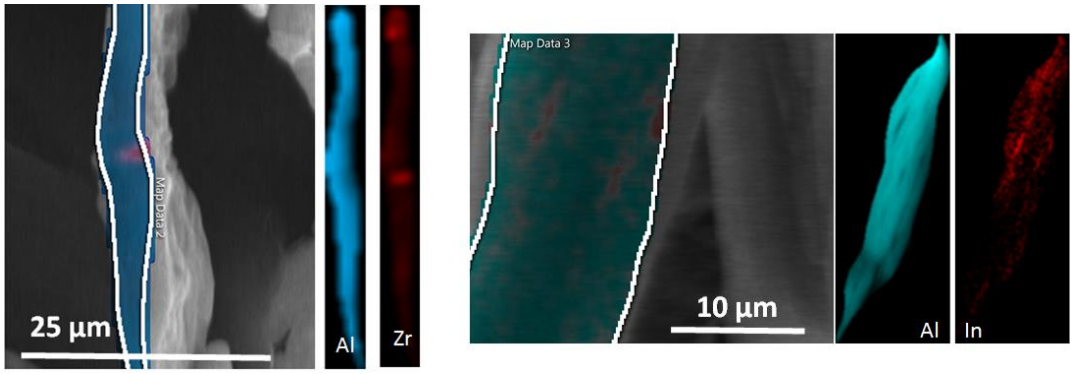

Fig. 3 EDS maps for the used powders left: MA Al90Zr10 right: MAAl90In10

The XRD pattern of the prepared powders showed sharp peaks of either of the contributing metals. This showed that the milling procedure does not produce any intermetallic nor that aluminum absorb any of the other inclusion in solid solution. but it is merely a composite particles contain both elements which is in agreement with EDS maps from FIBs

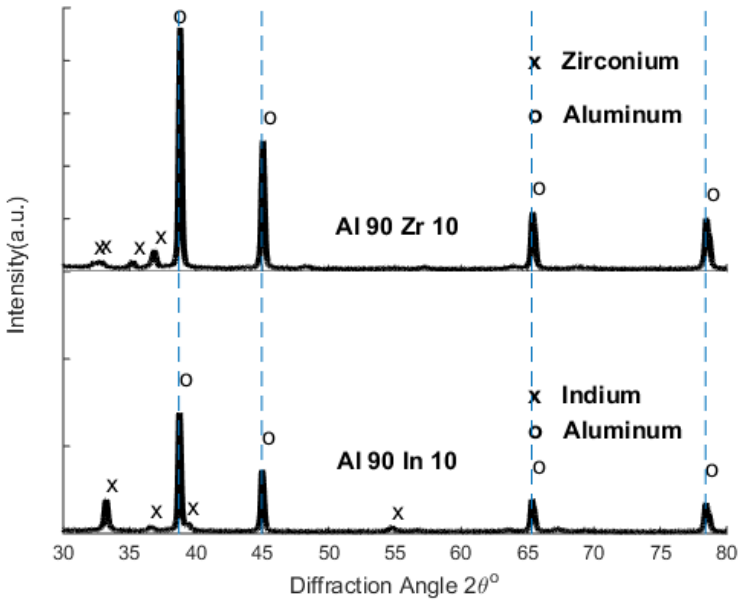

Fig. 3 XRD patterns of prepared powder Al90In10 and Al90Zr10

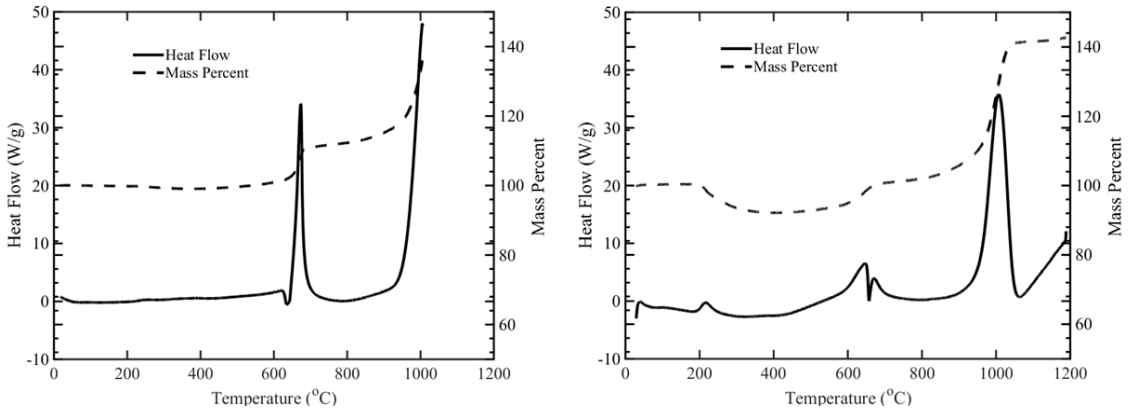

Fig. 4 DSC/TGA from 100 to 1000°C (20 K/min, 20/80 vol% O2/Ar) of Al90In10 (left) and Al90Zr10 (right)

DSC/TGA results for the Al with 10% In. milled material didn't show that initial exotherm at 230oC, as did the Al90In10 milled for 30 min only, so all the Indium is diffused into the Al during milling. The mixture starts melting at 627oC near the eutectic melting at 638 oC. The exotherm after that is related to oxidation. This also shows later oxidation stages but not as dominant as the previous one as a lot of Al have oxidized already.

For Al90Zr10 there is a slight exotherm at 200 oC. associated mass loss. most probably of HDPE contamination form the milling container. However, the material starts to oxidize with a exotherm onset at 550-600 oC. but not very rapidly, as the endotherm from Al melting at around 660 oC can be seen., that means almost no diffusion of Zr into Al which is in agreement with EDS maps shown in Fig.3. From the phase diagram [77] , The solubility limit for Zr in Al is 0.14% . so at heating it forms an intermetallic, probably Al3Zr. which This melts at 1850 K which beyond the capability of DSC/TGA used in this experiment.,. Large exotherm centered at 1000C is from liquid Al oxidizing. Form cooling curve, it can be noticed that there is a little exothermic pump indicating, the remaining Al solidifying again

The ignition experiment was done using CO2 laser, and the peak incident irradiance was controlled through a ZnSe focusing lens with a focal length of 50 cm. each point in Fig.5 is average of 5 points with the error bars are 1 standard deviation form that means.

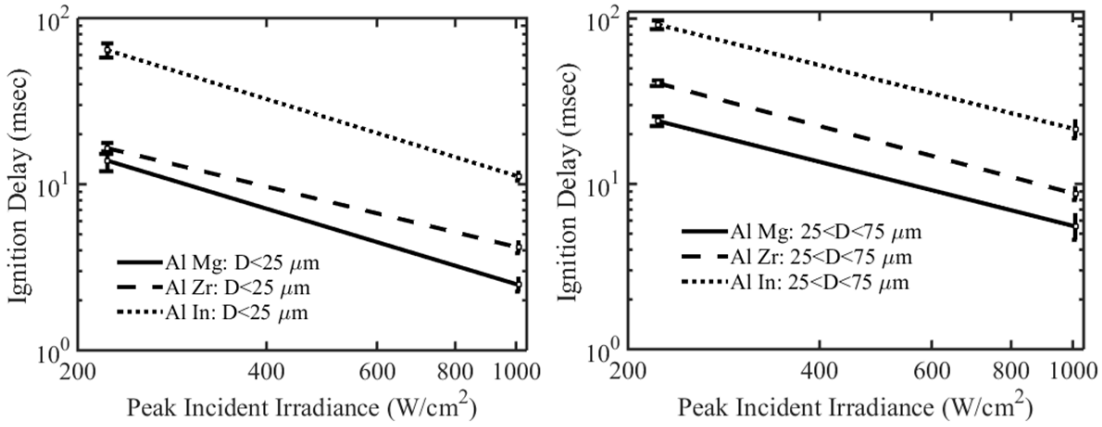

Fig. 5 Ignition delay times for Al90Zr10 and Al90In10 in comparison to Al90Mg10(MA90) [33] powders. Left: particles < 25 micron, Right: particles sieved between 25-75 micron

From Fig.5, the mechanical activation process is succeeded in change reactivity of aluminum which at the same peak irradiance does not ignited. However, this reactivity depends on the metal inclusion, being Mg -inclusion gives the lowest ignition delay times and In-inclusion is the largest ignition times.

Burning of strands of propellant mixed using the prepared powders, and as long as equivalent weight of physical mixture of pure elements (physical mixture of 90% Al and 10% either Indium or Zirconium.) were done in windowed pressure vessels..

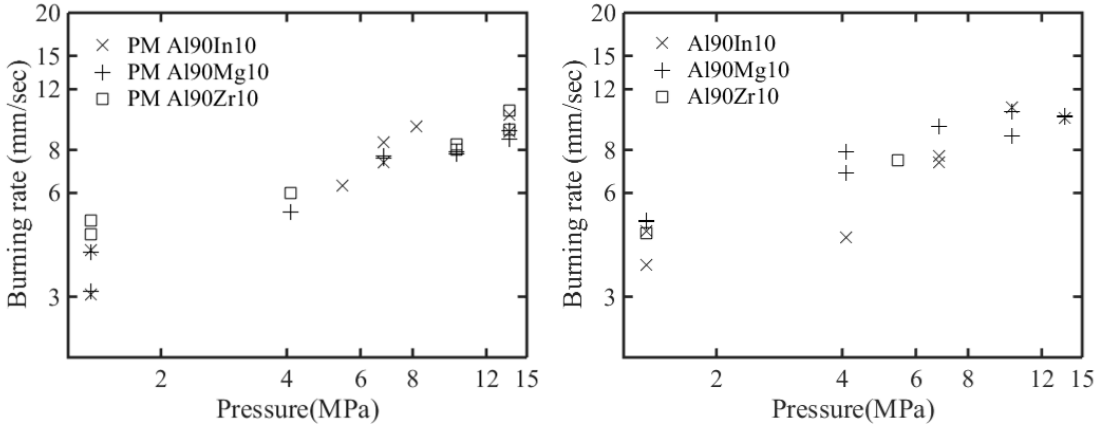

Fig. 6 Burning rates for solid propellant with magnesium, Zirconium /Indium inclusion, Left: physical mixture of Al/Mg., Al/In and Al/Zr Right MA Al/Mg , AL/In and Al/Zr composite powder

Linear burning rate for these propellant was evaluated using image processing of high speed videos captured at 5000 frame/sec. The results showed no statistically significant variation in burning rate as the difference is within burning rate uncertainty

In addition to burning rates, capturing of condensed phase products emerging from burning stands from propellant contain either MA-Al90Zr10 or Al90In10 MA powders or physical mixture of the same ratio at ambient condition showed that in comparison to neat aluminum propellant, only physical mixture of Al and Zr gives lower agglomeration size

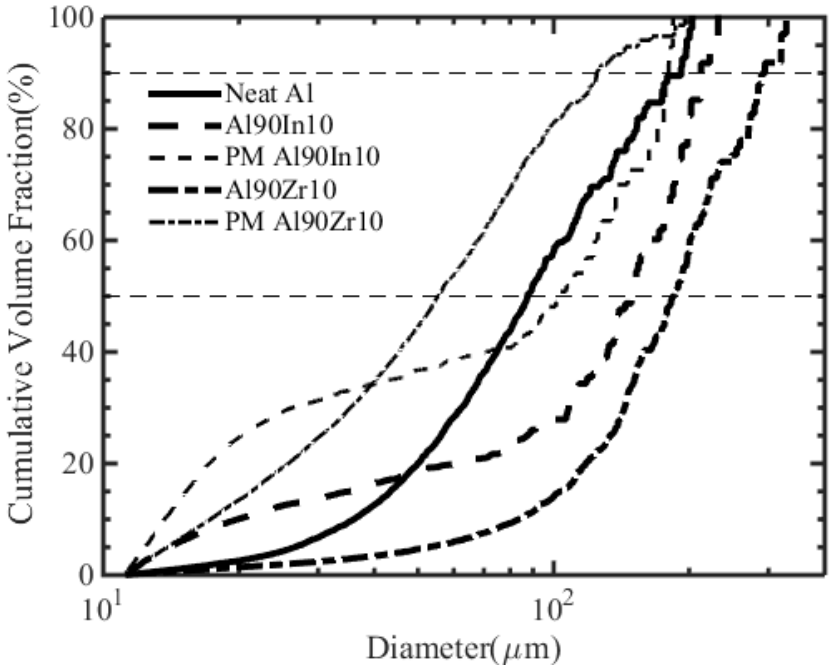

Fig. 7 Cumulative Volume fraction for condensed phase products for solid propellant with magnesium, Zirconium /Indium inclusion, collected in air at atmospheric pressure

This result is not surprised as for small level of other inclusion there will be no large scale heterogeneous structures observed previously for high magnesium inclusion (50%) with aluminum [61]. In addition, the high energy SPEX milling results in very thin flakes shapes which are known to have were shown previously that they have lower ignition temperature than spherical shape particles but have higher tendency to agglomerate with each other's at propellant surface.

5.4 Conclusion

Aluminum reactivity can be tailored using different metal inclusions starting from reactive metals such ass magnesium and zirconium to the less reactive ones like indium.

Effectiveness of metal inclusion in agglomeration reduction (especially at low inclusion level 10% and lower) depends milling procedure and mainly on particle morphology. As using high energy milling machine as SPEX8000 results in very thin flake shape particles (even with changes of operation cycle) while for the same active milling time on a Planetary milling operate at low speed (200 rpm) it results in flake shape with micron thickness which have better performance considering burning rate enhancement or agglomeration size reduction

CHAPTER 6. CONCLUSIONS AND FUTURE WORKS

6.1 Conclusion

Aluminum reactivity can be tailored using different metal inclusions starting from reactive metals such ass magnesium and zirconium to the less reactive ones like indium with mechanical milling/alloying proved to be effective way to increase reactivity of brittle (e.g. intermetallic as magnalium) or ductile materials (e.g. aluminum and magnesium).

Metastable mechanically activated showed higher reactivity than the alloy with the same weight ratio. The MA Al-Mg powders reacts before melting which is preferred to get lower agglomeration size. Flake particles have higher tendency to agglomerate than spherical particles, this is shown for MA powder for size range less than 25 microns., Lower ignition particles showed small agglomerates

A new particle shattering mechanism that results in large reduction of agglomeration size was discovered, this mechanism is responsible for reducing agglomeration size at high pressure when the classical microexplosion mechanism cease to act.

As a compromise between loss of specific impulse and gain in specific impulse due to lower two phase losses as magnesium percentage increase. MA70 may be suggested as the optimum composition combining the loss in specific impulse (-2 sec) with the reduction in agglomeration size (30% compared to 40%) which not justify the loss in theoretical specific impulsEffect of magnesium percent on burning rate of aluminized solid propellant depends whether this magnesium in physical mixture state or in MA state. For MA, increase Mg% results in increase in burning rate up to 50% magnesium however, the behavior is reversed in case of physical mixture. In MA case, the whole particle ignites at propellant surface which increase the amount of heat energy in condensed phase, but in physical mixture, the ignited magnesium particles result in lower flame temperature which decrease heat

feedback to propellant surface which counteract the increased heat release in condensed phase

Effectiveness of metal inclusion in agglomeration reduction (especially at low inclusion level 10% and lower) depends milling procedure and mainly on particle morphology. As using high energy milling machine as SPEX8000 results in very thin flake shape particles (even with changes of operation cycle) while for the same active milling time on a Planetary milling operate at low speed (200 rpm) it results in flake shape with micron thickness which have better performance considering burning rate enhancement or agglomeration size reduction

6.2 Future Work.

Future work should investigate

Investigate combustion efficiency of solid propellant contain MA Al-Mg in small scale motor to verify the effect of lower agglomeration size.

MA Al-Mg at low magnesium content and for longer milling time at low speed in order to achieve more diffusion of metals which may result in higher probability of particle shattering.

Investigate Mechanical milling of aluminum with aluminum rather than magnesium in order to increase yield of milling procedure

Modify milling procedure for Indium and Zirconium either by using process control agent (PCA) to decrease cold welding or change milling device to be planetary milling and perform at low speed, or in order to get particles morphology that can be better for agglomeration reduction.

LIST OF REFERENCES

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1. Y.M. Timnat Advanced Chemical Rocket Propulsion, Academic Press 1987
2. K. Jayaraman; K. V. Anand; David S. Bhatt; Satyanarayanan R. Chakravarthy; R. Sarathi Production, Characterization, and Combustion of Nanoaluminum in Composite Solid Propellants Journal of Propulsion and Power, Vol. 25, No. 2, pp. 471-481 (2009)
3. Y. Yavor, A. Gany, Effect of nickel coating on aluminum combustion and agglomeration in solid propellants, in: 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Hartford, CT, 2008.
4. O. G. Glotov, D. A. Yagodnikov, V. S. Vorob'ev, V. E. Zarko, V. N. Simonenko Ignition, combustion, and agglomeration of encapsulated aluminum particles in a composite solid propellant. II. Experimental studies of agglomeration Combustion, Explosion, and Shock Waves, Volume 43, Issue 3, pp 320–333 (2007)
5. D.A. Reese, L.J. Groven, S.F. Son, A.S. Mukasyan, Intermetallic compounds as fuels for composite rocket propellants, in: 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Diego, CA, 2011.
6. Sara Cerri, Manfred A. Bohn,Klaus Menke and Luciano Galfetti Aging of HTPB/Al/AP Rocket Propellant Formulations Investigated by DMA Measurements Propellant, Explosives and PyrotechnicsVolume 38, Issue 2 Pages 190–198 (2013)
7. V.A. Babuk, V.A. Vassiliev, V.V. Sviridov, in: V. Yang, T.B. Brill, W.Z. Ren, P.Zarchan (Eds.), Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics AIAA, 2000, p. 749–776.
8. V. Me Ivanov and P. I. Nefedov Experimental investigation of the combustion process of natural and emulsified liquid fuels NASA TT F-258 (1965)

9. J.C. Lasheras, A.C. Fernandez-Pello and F.L.Dryer Experimental Observations on the Disruptive Combustion of Free Droplets of Multicomponent Fuels Combustion Science and Technology 22 195-209. (1980)
10. Lasheras, J. C., Fernandez-Pello, A. C., Dryer, F. L.Dryer Initial Observations on the Free Droplet Combustion Characteristics of Water-In-Fuel Emulsions Combustion Science and Technology 21 1-4. (1979)
11. Masato Mikami, Takashi Yagi and Naoya Kojima Occurrence probability of microexplosion in droplet combustion of miscible binary fuels Proceedings of the Combustion Institute, 27, 1933-1941 (1998).
12. C. Shen , W.L. Cheng and C.F. Lee Micro-Explosion Modeling of Biofuel-Diesel Blended Droplets SAE paper 2011-01-2011 (2011)
13. C.K. Law and F.A. Williams Combustion of Magnesium particles in oxygen-inert atmospheres Combustion and flame Vol. 22 pp383-405 (1974)
14. P. Bucher, R.A. Yetter. F.L. Dryer and E.P. Vicenzi Condensed pjase species Distribution about AL particles reacting in various oxidizer Combustion and Flame Volume 117 pp351-361 (1999)
15. A. L. Breiter, L. Ya. Kashporov, V. M. Mal'tsev, P. F. Pokhil, E. I. Popov, V. I. Pepe kin, and A. G. Stasenko Combustion of individual aluminum-magnesium alloy particles in the flame of an oxidizer-fuel mixture, Volume 7, Issue 2, pp 186–190 (1971)
16. A.W. Blackman and D.K. Kuehl Use of Binary light metal mixtures and alloys as additives for solid propellants, American Rocket Societey Journal Vol 31 P1265-1272 (1961).
17. Narendra N. Dea, , Nicholas R. Cummocka, Ibrahim E. Gunduza, Bryce C. Tappanb, Steven F. Sona Photoflash and laser ignition of select high-nitrogen materials Combustion and Flame Volume 167, Pages 207–217 (2016)
18. Travis R. Sippel ,, Steven F. Son, Lori J. Groven Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles Combustion and Flame 161 311–321(2014)

19. J.L. Murray Phase Diagrams of Binary Magnesium Alloys. ASM International metals Park pp17-34 (1988)
20. Y. H. Yen Numerical and Experimental study of breakup process in solid rocket motor nozzle. Dissertation, The University of Wisconsin Milwaukee 2016
21. R. Houim, E. Boyd and K.K. Kuo Combustion of Aluminum Flakes in the post flame zone of hencken burner International Journal of Energetic Materials and Chemical Propulsion Volume 7, 2008 Issue 1 > C pp pages 55-71 (2008)
22. Kubota, N., and Serizawa, C., "Combustion of Magnesium Polytetrafluoroethylene", Journal of Propulsion and Power, Vol. 3, No. 4, ,pp. 303-307 (1987)
23. A. Ishihara and M.Q. Brewster Combustion Studies of Boron, Magnesium, and Aluminum Composite Propellants Combustion science and Technology Vol. 87 pp275-290 (1992)
24. T.L. Sheridan Combustion Studies of magnesium Ammonium Nitrate Propellants , Master Thesis , University of Illinois at Urbana Champaign
25. T. A. Roberts, R. L. Burton and H. Krier Ignition and Combustion of Aluminum / Magnesium Alloy Particles in O2 at High Pressures Combustion and Flame Vol. 92 pp 125-143 (1993).
26. T. W. Megli Aluminum Magnesium particle ignition in shocked mixtures of water vapor and argon Master Thesis University of Illinois at Urbana-Champaign 1993
27. M. Quinn Brewster and Brian E. Hardt Influence of Metal Agglomeration and Heat Feedback on Composite Propellant Burning Rate Journal of Propulsion and Power Vol.7 No. 6 pp 1076-1078 (1991).
28. R.-H. Chen,C. Suryanarayana, and M. Chaos Combustion Characteristics of Mechanically Alloyed Ultrafine-Grained Al-Mg Powders Advanced engineering materials Volume 8, Issue 6 pp563–567 (2006)
29. V. R. PAl VERNEKER, SAROJINI DEEVI, and SEETHARAMA C. DEEVI Role of Alloys in the Thermal Decomposition and Combustion of Ammonium Perchlorate Combustion and Flame Vol 67:163-173 (1987)

30. Daniel A. Rodriguez a, Edward L. Dreizin b, Evgeny Shafirovich Hydrogen generation from ammonia borane and water throughcombustion reactions with mechanically alloyed AlMg powder Combustion and Flame Vol. 162 1498–1506 (2015)
31. Yasmine Aly, Vern K. Hoffman, Mirko Schoenitz, and Edward L. Dreizin. "Reactive, Mechanically Alloyed Al·Mg Powders with Customized Particle Sizes and Compositions", Journal of Propulsion and Power, Vol. 30, No. 1 (2014), pp. 96-104.
32. Amy L. Corcoran, Song Wang, Yasmine Aly & Edward L. Dreizin (2015) Combustion of Mechanically Alloyed Al·Mg Powders in Products of a Hydrocarbon Flame, Combustion Science and Technology, 187:5, 807-825
33. Hatem Belal, Chang Wan Han, I. Emre Gunduz, Volkan Ortalan and Steven F. Son Behavior of Mechanically Activated Al-Mg particles in Composite Solid Propellants " (in preparation)
34. Narendra N. De, , Nicholas R. Cummocka, Ibrahim E. Gunduza, Bryce C. Tappanb, Steven F. Sona Photoflash and laser ignition of select high-nitrogen materials Combustion and Flame Volume 167, Pages 207–217 (2016)
35. Travis R. Sippel ,⇑, Steven F. Son, Lori J. Groven Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles Combustion and Flame 161 311–321(2014)
36. L.E. Fried, W.M. Howard, P.C. Souers, P.A. Vitello, Cheetah 6.0 User Manual,Report No. LLNL-SM-416166, Lawrence Livermore National Laboratory, 2010
37. R. M. Muthiah, V. N. Krishnamurthy, and B. R. Gupta Rheology of HTPB propellant. I. Effect of solid loading, oxidizer particle size, and aluminum content Journal of Applied Polymer Volume 44, Issue 11 pp 2043–2052 (1992).
38. C.W. Fong, R.F. Smith The relationship between plateau burning behavior and ammonium perchlorate particle size in HTPB-AP composite propellant Combustion and Flame Volume 67, Issue 3, March 1987, Pages 235-247
39. Magnalium a new alloy American Jeweler Vol 28 pp541 (1908).

40. G.J.Mills et al. Propellant fuel containing magnesium aluminum alloy US patent 3180770 (1965)
41. Naofumi Negishi and Takuo Kuwahara. "Effects of Mg-Al Particle Additions on Combustion Characteristics of Ducted Rockets", 51st AIAA/SAE/ASEE Joint Propulsion Conference, Propulsion and Energy Forum, (AIAA 2015-4235)
42. TSUJIKADO, NOBUO; KASHIKAWA, IWAO; Harada, Tadamasa; Anan, Toshiyuki Experimental studies on solid propellant type fuels for ram-rocket - Improved propellant formulations for efficient boron combustion International Symposium on Air Breathing Engines, 9th, Athens, Greece; UNITED STATES; 3-8 Sept. 1989. (1989).
43. H. MURATA and HORI Enhancement of the combustion characteristics of AN based composite propellant with Mg-Al 34th International Annual Conference of ICT June 24 - June 27, 2003 Karlsruhe, Federal Republic of Germany pp-158-1:158-12 ( )
44. Xiong-Gang Wu,Qi-LongYan, Xin Guo,Xiao-Fei Qi,Xiao-Jiang Li,Ke-Qiang Wang Combustion efficiency and pyrochemical properties of micron-sized metal particles as the components of modified double-base propellant Acta Astronautica Vol 68 pp1098–1112 (2011).
45. Qi Xiao fei, Zhang Ziao hong, Song Zhen wei, Yan Qi-long Liu Fang Li and Li Jun qiang Combustion chracteristics of CMDB Propellant Containing Mg/Al Mechanical alloy Chinses Journal of explosives and proepllants Vol. 35 Issue 6 pp-81-85 (2012)
46. Habu, Hiroto; Sato, Wataru; Komai, Iwao; Hori, Keiichi; Saito, Takeo; Successful firong of sub scale motors loaded with magnalium AP composite propellant Proceedings of the twenty-third international symposium on space technology and science , Japan Society for Aeronautical and Space Sciences, Tokyo, (2002).
47. Habu, H; Hori, K; Saito, T; Kohno, M The combustion mechanism of AP based propellant containing magnalium Energetic materials - Ignition, combustion and detonation, Karlsruhe, Germany; GERMANY; 3-6 July 2001.
48. Yuriy L. Shoshina, Ruslan S. Mudryya, Edward L. Dreizin Preparation and characterization of energetic Al-Mg mechanical alloy powders Combustion and Flame Volume 128, Issue 3, February 2002, Pages 259–269

49. Mirko Schoenitz¤ and Edward L. Dreizin Emil Shtessel Constant Volume Explosions of Aerosols of Metallic Mechanical Alloys and Powder Blends Journal of Propulsion and Power Vol. 19, No. 3,(2003)
50. X. Kang, F. Yang, J. Luo and Y. Tang Thermal Ignition and Combustion Behavior of Pyrotechnic Composition Containing Mechanically Activated Commercial Mg Al Alloy Combustion Science and Technology, 187:6, 963-975
51. C.C. Koch Amorphization of single composition powders by mechanical milling Scripta Materialia Volume 34, Issue 1,Pages 21-27 (1996).
52. D. Yu. Kovalev,1 N. A. Kochetov,1 and V. I. Ponomarev Criteria of the Critical State of the Ni–Al System during Mechanical Activation Combustion, Explosion, and Shock Waves, Vol. 46, No. 4, pp. 457–463, 2010
53. G. Mohan and F.A. Williams Ignition and Combustion of Boron in O2/Inert Atmospheres AIAA Journal Vol.10 No. 6 pp776-783 (1972).
54. Travis R. Sippel ,, Steven F. Son, Lori J. Groven Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles Combustion and Flame 161 311–321(2014)
55. Hai-Tao Huang , Mei-Shuai Zou , Xiao-Yan Guo , Rong-Jie Yang , Yun-Kai Li , En-Zhou Jiang & Zhong-Shan Li Study of Different Al/Mg Powders in Hydroreactive Fuel Propellant Used for Water Ramjet, Journal of Energetic Materials, 32 32:sup1, S83-S93 (2014).
56. A. Zolriasatein, , A. Shokuhfar Size effect on the melting temperature depression of Al12Mg17 complex metallic alloy nanoparticles prepared by planetary ball milling Physica E: Low-dimensional Systems and Nanostructures Volume 74, November , Pages 101–107 (2015).
57. Hatem Belal, Chang Wan Han, I. Emre Gunduz, Volkan Ortalan and Steven F. Son Behavior of Mechanically Activated Al-Mg particles in Composite Solid Propellants “ in preparation
58. Travis R. Sippel ,, Steven F. Son, Lori J. Groven Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles Combustion and Flame 161 311–321(2014).

59. D.A. Reese, L.J. Groven, S.F. Son, A.S. Mukasyan, Intermetallic compounds as fuels for composite rocket propellants, in: 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, San Diego, CA, 2011.
60. Hatem Belal, Chang Wan Han, I. Emre Gunduz, Volkan Ortalan and Steven F. Son Behavior of Mechanically Activated Al-Mg particles in Composite Solid Propellants “ (in preparation)
61. Kenneth K. Kuo Martin J. Chiaverini , "Metals, Energetic Additives, and Special Binders Used in Solid Fuels for Hybrid Rockets", Fundamentals of Hybrid Rocket Combustion and Propulsion, Progress in Astronautics and Aeronautics, pp. 413-456.
62. M. K.King and J.M. Semple Ignitio and combustion of zirconium particles used in solid propellant formulation CPIA 273 12th JANNAF Combustion meeting Vol II pp221 (1975)
63. Takeshi Suzuki, Takaki Odawara, Kengo Kunitou, Mitsuaki Tanabe, and Takuo Kuwahara. "Combustion and Ignition Characteristics of Zr in Solid Fuel of Ducted Rockets", 40th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Joint Propulsion Conferences
64. C. N. Divekar, S. N. Asthana, and Haridwar Singh. "Combustion and Thermal Studies on Al/Ti/Ni/Zr Composite Modified Double-Base Systems", Journal of Propulsion and Power, Vol. 19, No. 4 (2003), pp. 614-622.
65. C. N. Divekar, S. N. Asthana, and Haridwar Singh. "Studies on Combustion of Metallized RDX-Based Composite Modified Double-Base Propellants", Journal of Propulsion and Power, Vol. 17, No. 1(2001), pp. 58-64.
66. B.K.Athavale, S.N.Asthana, P.G.Shrotri and Haridwar Singh Combustion Studies on metallized composite and composite modified double base propellants Proceedings of the XII I National Conference on IC Engines and Combustion, Bangalore, 18-20 January 1994.
67. Byoung-Sun Min and Hyung Soo Hyun. "Study on Combustion Characteristics and Performance of HTPB/AP Propellants Containing Zirconium", Journal of Propulsion and Power, Vol. 28, No. 1 (2012), pp. 211-213.

68. Brewster, M. Q., and Hardt, B. E., “In• uence of Metal Agglomeration and Heat Feedback on Composite Propellants Burning Rate,” Journal of Propulsion, Vol. 7, No. 6, 1991, pp. 1076–1078.
69. A. P. Alekseev, D. B. Lempert, G. G. Nemtsev, G. N. Nechiporenko Combustion of zirconium-containing model compositions of solid propellant Russian Journal of Physical Chemistry B Volume 5, Issue 6, pp 997–999 (2011)
70. D. B. Lempert, M. Brambilla and L. T. DeLuca Ballistic effectiveness of Zr-containing composite solid propellants as a function of binder nature and mass fraction Progress in Propulsion Physics 4 pp15-32 (2013)
71. Hao Fu1, Hui Zou1, Shui-zhou Cai The role of microstructure refinement in improving the thermal behavior of gas atomized Al-Eu alloy powder Advanced Powder Technology (2016) In Press, Corrected Proof
72. C. Johnson, T. Parr, D. Hanson-Parr, R. Hollins, S. Fallis, and K. Higa, Combustion and Oxidation of Metal Nanoparticles and Composite Particles, Proc. 37th JANNAF Combust. Subcom. Meeting, 13–17 November, 2000, pp.539..
73. S. H. Gelles and A. J. Mark worth. "Microgravity Studies in the Liquid-Phase Immiscible System: Aluminum-Indium", AIAA Journal, Vol. 16, No. 5 (1978), pp. 431-438.
74. R. T. Meyer AND L. S. Nelson The Role of Nitrogen in the Formation of Microbubbles During the Explosive Combustion of Zirconium Droplets in N 2/02 Mixtures HJGH TEMFERATURE SCIENCE~ 35-57 (1970)
75. Narendra N. Dea, , Nicholas R. Cummocka, Ibrahim E. Gunduza, Bryce C. Tappanb, Steven F. Sona Photoflash and laser ignition of select high-nitrogen materials Combustion and Flame Volume 167, Pages 207–217 (2016)
76. ASM Handbook Vol 3 Alloy Phase Diagram, ASM International (1992)

VITA

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