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Characterization of an Aluminum-Lithium Alloy Based Composite Propellant at Elevated Pressures

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CHARACTERIZATION OF AN ALUMINUM-LITHIUM ALLOY BASED COMPOSITE PROPELLANT AT ELEVATED PRESSURES

by

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A Thesis

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THE PURDUE UNIVERSITY GRADUATE SCHOOL
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        Head of the Graduate Program

To my parents Jorge and Carmen, to whom I owe everything.

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ABSTRACT

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Aluminum-lithium (Al-Li) alloys have demonstrated a mechanism to improve composite propellant performance by reducing agglomerates through microexplosions. In addition, use of Al-Li significantly reduces hydrochloric acid production in ammonium perchlorate based propellants while also improving theoretical performance. Full combustion characterization (e.g., at various pressures) of the Al-Li based propellant has not been performed previously. Measurement of the aluminum-lithium composite propellant's burning rate and quantification of agglomerate production at various pressures is presented. Agglomerate size of the aluminum-lithium appeared to be smaller at lower pressures than at higher pressures, likely due to increased microexplosions at low pressures. Additionally, at high pressures the aluminum-lithium did appear to produce larger agglomerates than the aluminum, but upon closer inspection it was observed that the majority of these large agglomerates were liquid metal that had splashed off of the melt layer rather than condensed phase oxide products. This biased the aluminum-lithium samples towards larger agglomerate sizes without clear evidence the larger agglomerates would not burn given greater residence time and distance from the surface. Results show a pressure exponent of 0.29 for a composite propellant using aluminum-lithium powder sieved to 25-40 µm and 0.39 for a propellant using aluminum-lithium powder as-received. The difference in pressure exponents for the two powder sizes could be attributed to the greater microexplosivity increasing the burning rate at low pressures

CHAPTER 1. INTRODUCTION

1.1 Motivation & Background

Aluminum has been the most widely used fuel in solid rocket applications for decades. In composite propellants it has demonstrated an improvement in specific impulse (Isp) by as much as 15% [1]. However, during combustion the aluminum particles will tend to melt and agglomerate together on the burning surface, forming condensed product droplets of alumina (Figure 1.1) [2]. These agglomerated droplets lead to two-phase flow losses (non-equilibrium state between gas and condensed phases) and large enough liquid aluminum droplets can reduce performance in small motors due to decreased combustion efficiency. A great deal of research has been conducted to tailor aluminum particles to minimize their agglomeration during combustion [3,4,7,9]. Ammonium perchlorate (AP) based composite propellants also produce a significant amount of hydrochloric acid (HCl) which can corrode launch pads and contribute to ozone layer depletion [6,14]. Recently, aluminum-lithium alloys have been proposed as a replacement for aluminum

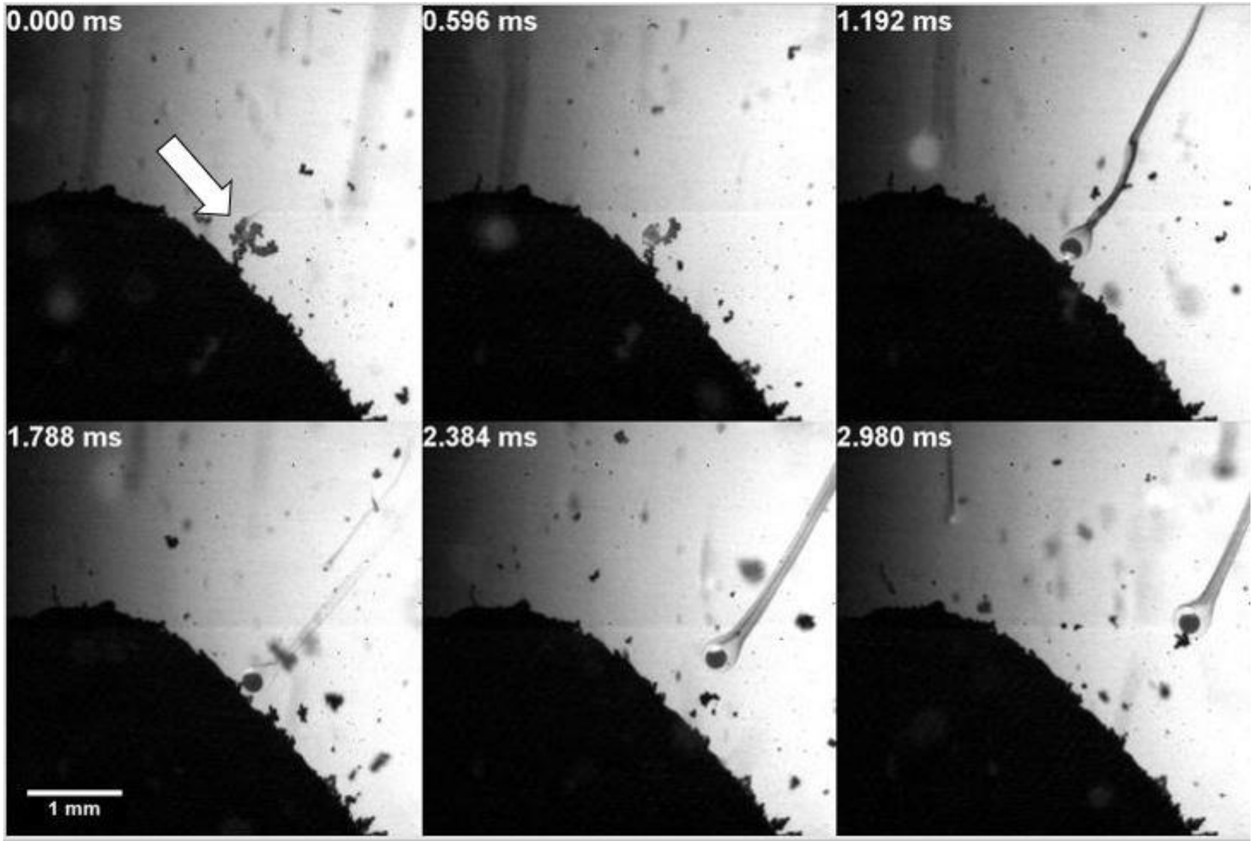


Figure 1.1 Formation of an agglomerated droplet on an aluminum propellant at 1 atm.

[5,6]. They have been proven to decrease HCl production, improve theoretical performance, and may also decrease agglomerate size [5,6].

Sambamurthi et al. (1984) demonstrated that reducing aluminum particle size created a more continuous dispersion among oxidizer particles within the packing array which led to more rapid combustion and less time for droplet agglomeration [2]. Early experiments on nano-aluminum based propellants did indeed demonstrate an improvement in burning rate, but the increase in surface area of the nano-powders meant aluminum oxide formation during storage and handling was more extensive which decreased the relative energy of the fuel [12]. More recently, studies involving the inclusion of fluoro- and hydrocarbon polymers such as polytetrafluoroethylene (PTFE) and low-density polyethylene (LDPE), respectively, within aluminum particles through mechanical activation have been conducted [3, 4]. Because of their lower boiling points, the polymers will rapidly expand and break apart the aluminum particles on which they are embedded, leading to the creation of new nano-scale features [3, 4]. However, the inclusion of additional inert polymers in a propellant led to a decrease in theoretical performance and the manufacturing of mechanically activated aluminum/fluoropolymer particles could be dangerous on a large scale since the fluoropolymer is an oxidizer of aluminum [4,5].

1.2 Aluminum-Lithium Alloy Fuels

The same microexplosions that occur from a difference in vaporization temperatures within two mechanically combined materials can also occur within metal alloys. Terry et al. (2016) studied a one-to-one atomic alloy of aluminum/lithium (Al-Li) and found that the lithium within the agglomerated liquid metal droplets will superheat (exceed its vaporization temperature) and then suddenly flash to vapor, shattering the droplet [5]. Additionally, theoretical calculations have shown that because of the lower molecular weight of lithium, Isp performance will also be improved because of the lower overall molecular weight of the products [6]. Finally, Al-Li propellants have been proven to reduce the amount of hydrochloric acid produced from propellants utilizing ammonium perchlorate (AP) as an oxidizer by reacting Li with HCl to form LiCl [6]. Although Al-Li shows great promise for improving both performance and environmentally friendliness, a quantitative assessment of its combustion performance, particularly as a function of pressure, is needed to properly compare it to other propellants.

1.3 Objective

The objective of this study is to measure the burning rate as a function of pressure and compare it to a standard aluminum propellant. In addition, a particle capturing technique was used to measure the effect of the microexplosions on the size of agglomerated product droplets as a function of pressure.

CHAPTER 2. EXPERIMENTAL METHODS

2.1 Propellant Formulation

Three solid composite propellants were fabricated with different metal fuels. Two of the propellants consisted of a one to one atomic aluminum-lithium alloy (80% Al, 20% Li), the metal powder was mixed as received for one propellant and sieved for 1 hour to a size range of 25-40 µm for the other. The third composite propellant consisted of neat as-received spherical aluminum (Valimet H30). The three powder's size distributions were determined through laser diffraction (Malvern Mastersizer Hydro 2000 µP). All three propellants were mixed with 15% metal, 15% binder, and 70% ammonium perchlorate (ATK, 20 µm and 200 µm, size distributions can be found in Ref. [13]) by weight with a 4:1 coarse-to-fine powder ratio used for the oxidizer. The binder consisted of 73.5% R45M HTPB (Rocket Motor Parts), 14.7% IDP plasticizer (Rocket Motor Parts), and 11.8% curing agent which was a modified methylene diphenyl diisocyanate (Rocket Motor Parts). Once the propellant constituents were combined and wetted with the binder, they were then submitted to resonant mixing (Resodyn LabRAM) at 80% intensity for 3 minutes. They were then cast inside 5.8 mm diameter by 6 cm long cylindrical molds and cured for 7 days at room temperature. The aluminum-lithium samples were cured inside an argon gas environment to prevent reaction with atmospheric humidity.

2.2 Particle Collection

Particle collection was performed using the quench disc method (Figure 2.1) described by Sippel et al. (2013) [3]. Strands of propellant were cut into 20 mm long pieces and a 25 mm diameter, 5 mm thick glass disk was loaded onto the mechanical arm. The strand was ignited using a Nickel-Chromium wire connected to a DC power supply. When the strand burned to a predetermined height it allowed a laser beam to pass through the pressure vessel and trigger a photo diode that reversed the polarity of the DC motor. The mechanical arm then swung over the surface of the burning propellant at a speed of about 7 m/s, collecting agglomerated particles on the glass disc about 1-6 mm above the burning surface of the propellant strands. A high speed color video camera (Vision Research Phantom v.10) was used to verify that the height of glass disc above the burning surface was within the desired range. The discs were then observed under a digital optical microscope (Hirox KH-8700) and composite images were taken of the particles that were captured. Using ImageJ, a binary contrast of each disc was produced in order to size the particles. Using ImageJ's built in particle selection, a distribution of particle surface areas was output from the software. These surface areas were used to calculate particle diameters under the assumption that all particles were mostly circular. In order to minimize the error of this assumption, only agglomerate particles with a circularity greater than 0.4 were analyzed.

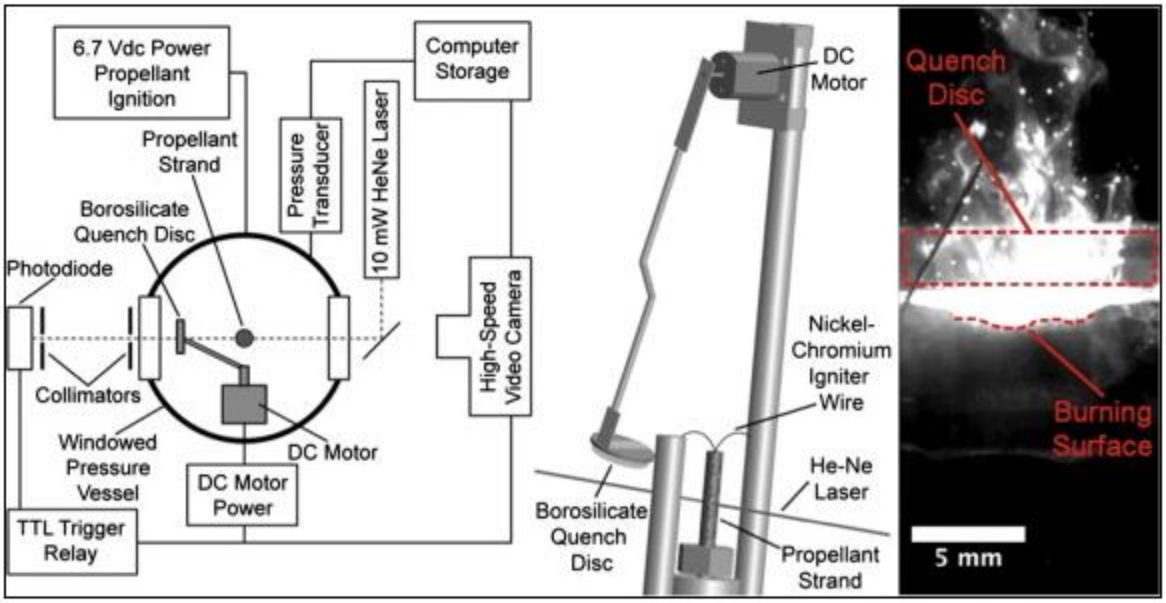


Figure 2.1 Diagram of particle collection experiment. When the burning strand reaches a certain height the laser beam triggers a photodiode that reverses the polarity of the DC motor. [3]

2.3 Burning Rate

Burning rate experiments were conducted in a vessel pressurized with nitrogen. The strands were cut into 1-2 cm long pieces, inhibited with a spray-on enamel coating (Rust-Oleum), and ignited with a Nickel-Chrome wire. The burning samples were filmed using a color high speed camera (Vision Research Phantom v.10) and the videos were analyzed in MATLAB using the regressing surface to measure the burning rate of the strand.

CHAPTER 3. RESULTS AND DISCUSSION

3.1 Propellant Mixing and Powder Characterization

Several different iterations were attempted before a final aluminum-lithium propellant formulation was selected for this study. Aluminum-lithium reacts readily with water, so the propellant had to be mixed in an environment with low humidity. It was determined that an absolute humidity below 3500 ppmv would lead to good mixing. Above this absolute humidity the composite propellants would cure poorly, forming large voids and burning inconsistently (large variance between measured burning rates) at each pressure tested. High humidity levels (>20,000 ppmv) led to rising temperatures and foaming from the mixture, indicating reaction with water. The initial particle size distribution of the spherical aluminum powder was between 10 µm and 100 µm (Figure 3.1) with a mean particle size of 33 µm. The size distribution of the as- received aluminum-lithium powder was much more spread out across size ranges starting at 1.7 µm and going up to 200 µm (Figure 3.1). The as-received aluminum-lithium was also coarser, with a mean particle diameter of about 53 µm. Although sieved aluminum-lithium was intended to be between 25 µm and 45 µm, many

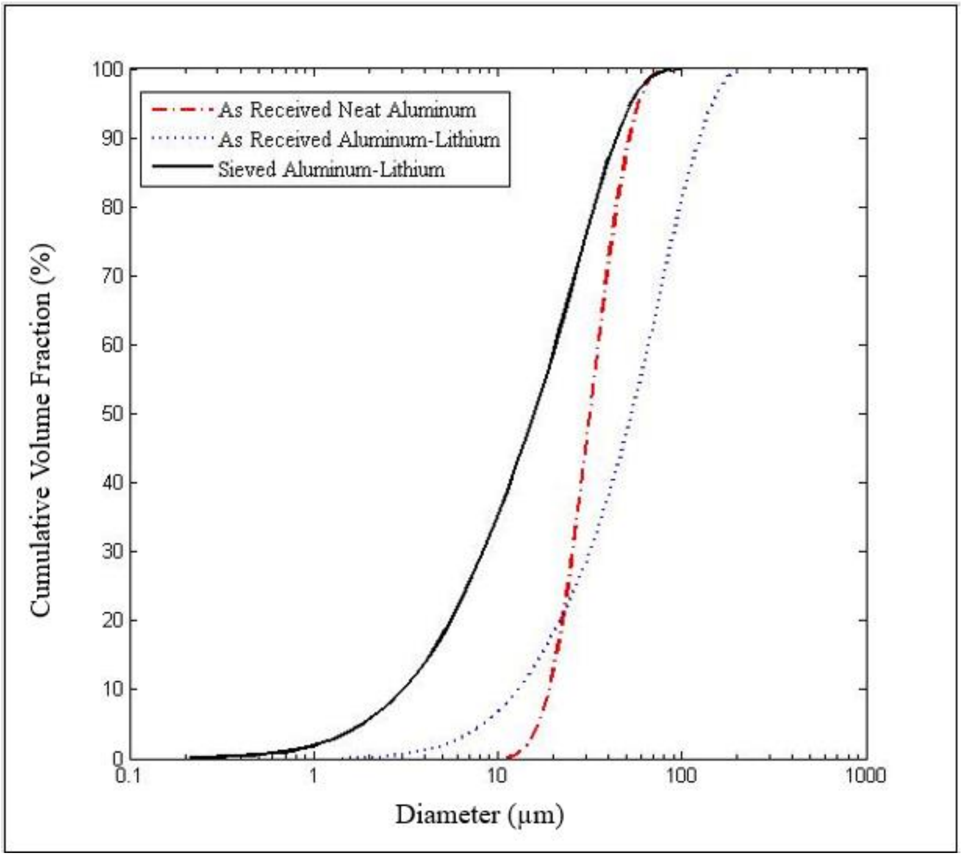


Figure 3.1 Size distribution of powders used in the propellants

of the finer particles were retained. As a result the size distribution appears similar to the as-received material though with most of the coarse particles removed . The result was a powder that was finer than the as-received aluminum, with a mean particle diameter of 17 μm.

3.2 Particle Collection

Particle collection experiments using the quench disk method were conducted at 0.34 MPa and 6.89 MPa and images taken of the disks are displayed in Figure 3.2. The images demonstrate qualitatively that although the sieved material was similar to the neat aluminum in initial particle size, the agglomerates produced at low pressure were significantly smaller. Additionally, although

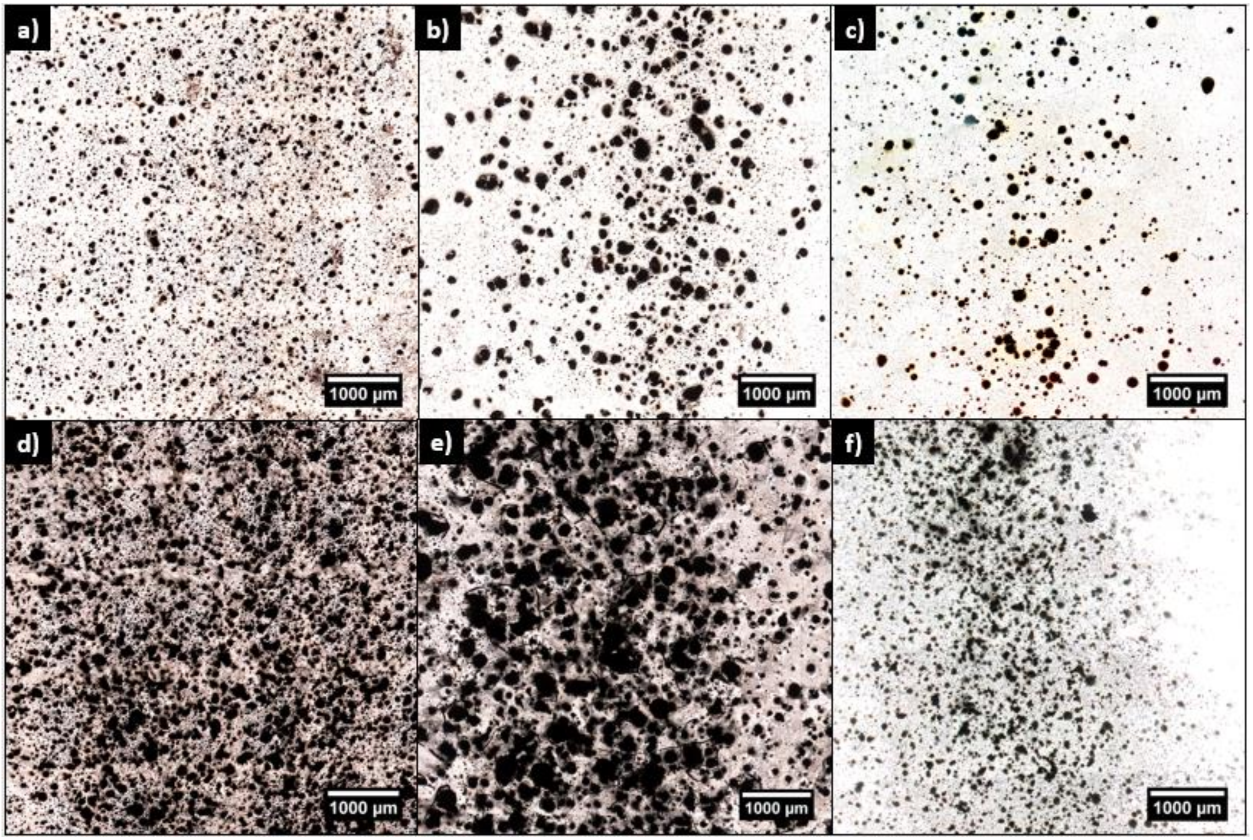


Figure 3.2 Agglomerated particles collected on a quench disk for sieved Al-Li , (a) and (d), as-received Al-Li, (b), and (e), and neat as received aluminum, (c) and (f). Propellants were burned at 0.34 MPa (top row) and 6.89 MPa (bottom row).

the as-received powder contained coarser particles than the aluminum powder, the agglomerates produced at low pressures appear to be comparable in size to the neat aluminum. At higher pressures, though, the trend is reversed. In a typical aluminum composite propellant such as the one tested, an increase in pressure will reduce agglomerate size since the higher burning rate provides less time for the condensed phase product to grow [2]. In the aluminum-lithium propellants, however, the increase in pressure lead to an increase in agglomerate size production. This effect can also be seen in the cumulative volume fractions of the materials (Figure 3.3).

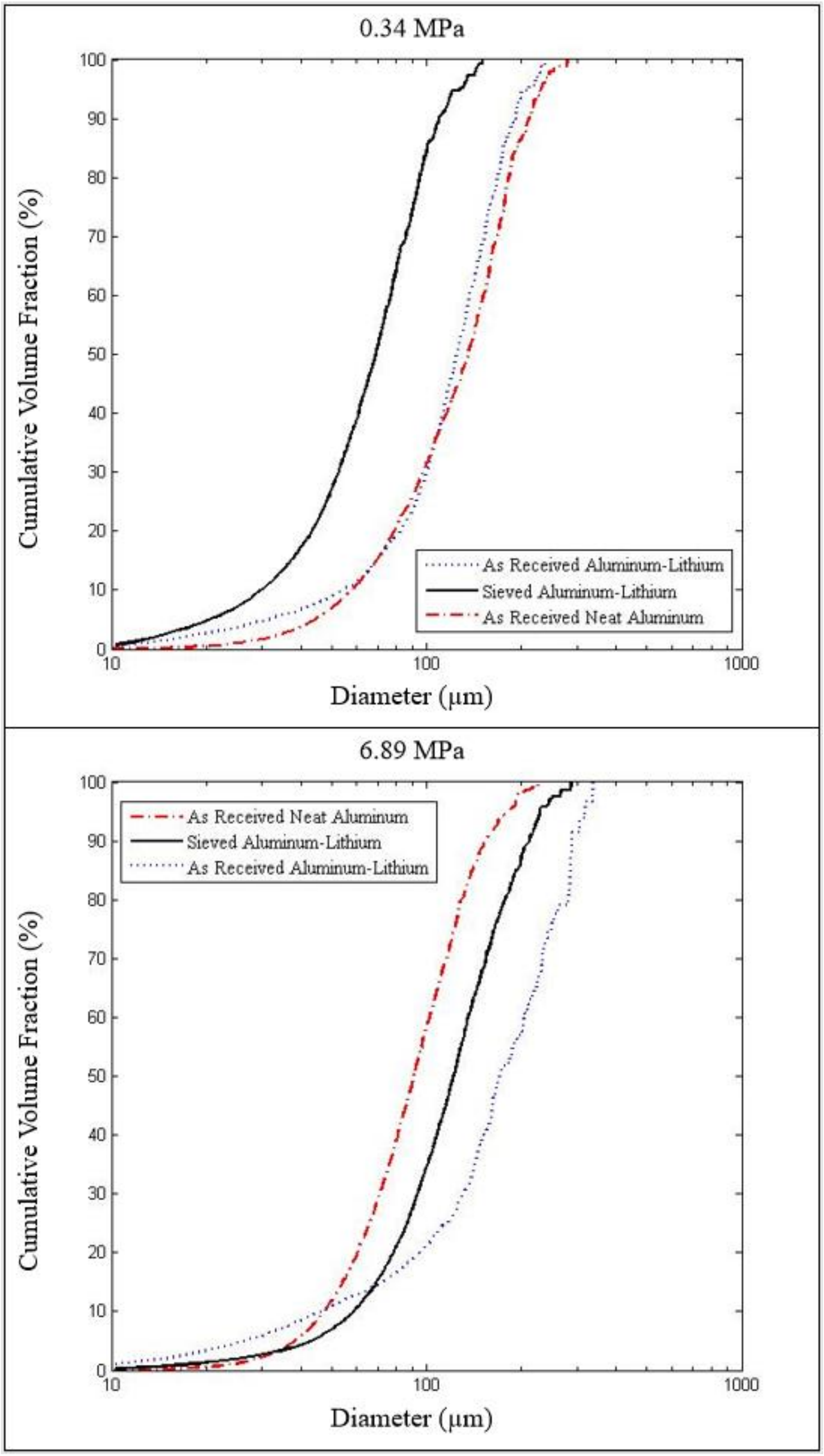


Figure 3.3 Agglomerate size distribution at 0.34 MPa (top) and 6.89 MPa (bottom)

Although about 10% of the as-received aluminum-lithium powder and about 35% of the sieved aluminum-lithium powder used in the propellant contained particle sizes below 10 μm, no

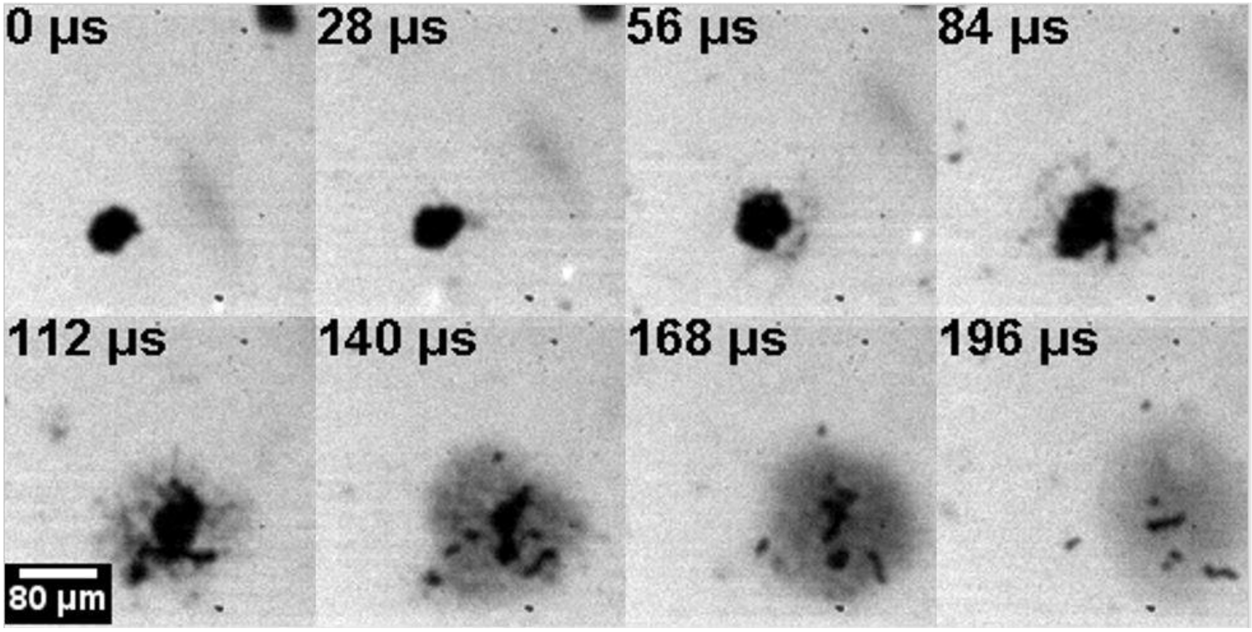


Figure 3.4 Time lapse of a microexplosion occurring at 1 atm.

agglomerates below 10 µm were considered in the analysis because they would be indistinguishable from smoke residue on image processing software.

The difference between the high- and low-pressure collected particles in the aluminum-lithium can be explained by the microexplosive behavior of the alloy. During combustion, the lithium on the droplet surface will burn more quickly, leaving a higher concentration of aluminum on the exterior of the liquid droplet [5]. If the core of the droplet is at a temperature higher than the boiling point of the lithium, then the droplet will experience uniform nucleation of lithium vapor and the entire droplet will shatter in a microexplosion (Figure 3.4)[5]. If the core of the droplet is below the boiling point of the lithium, then nucleation sites will occur in various

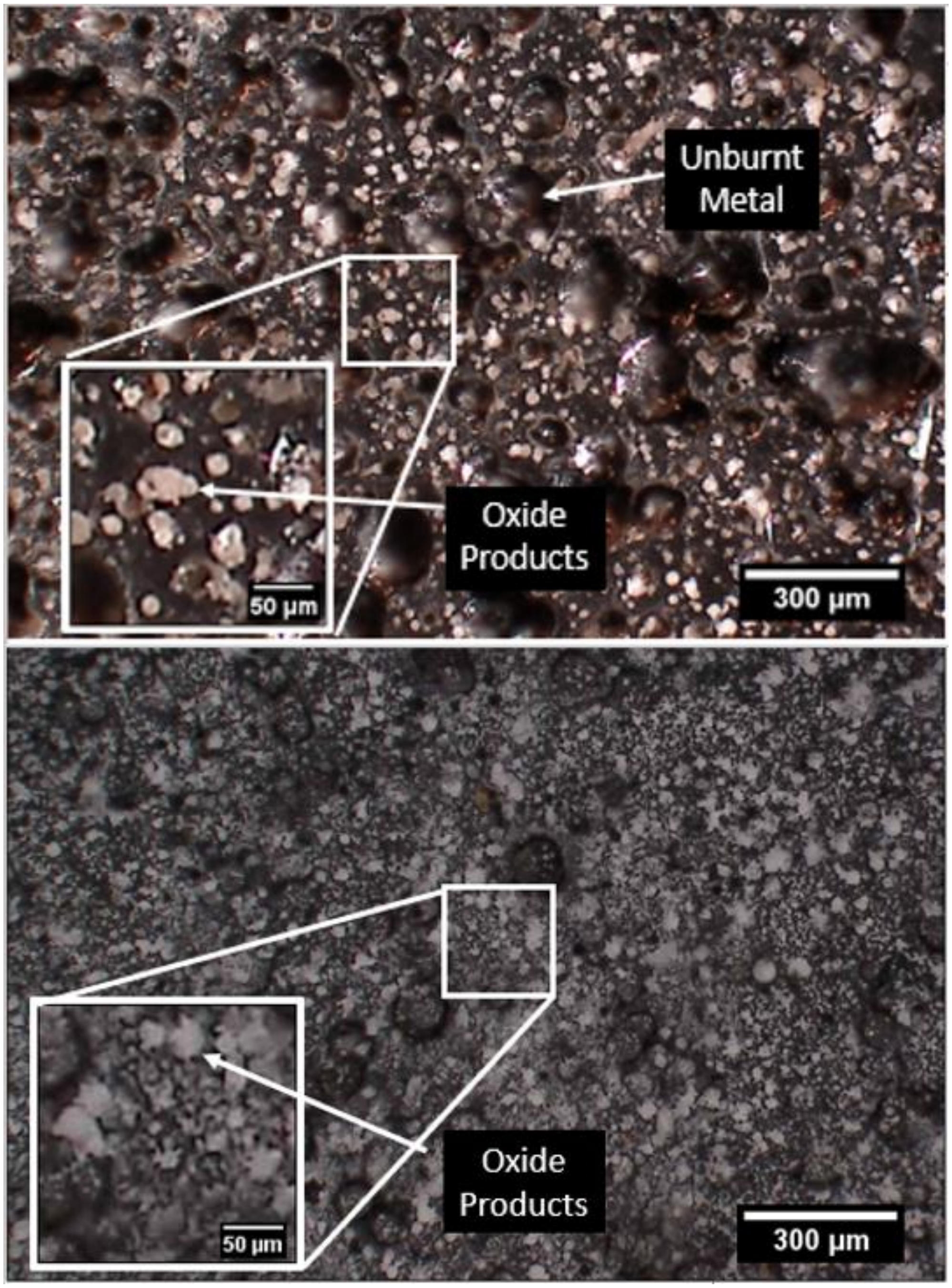
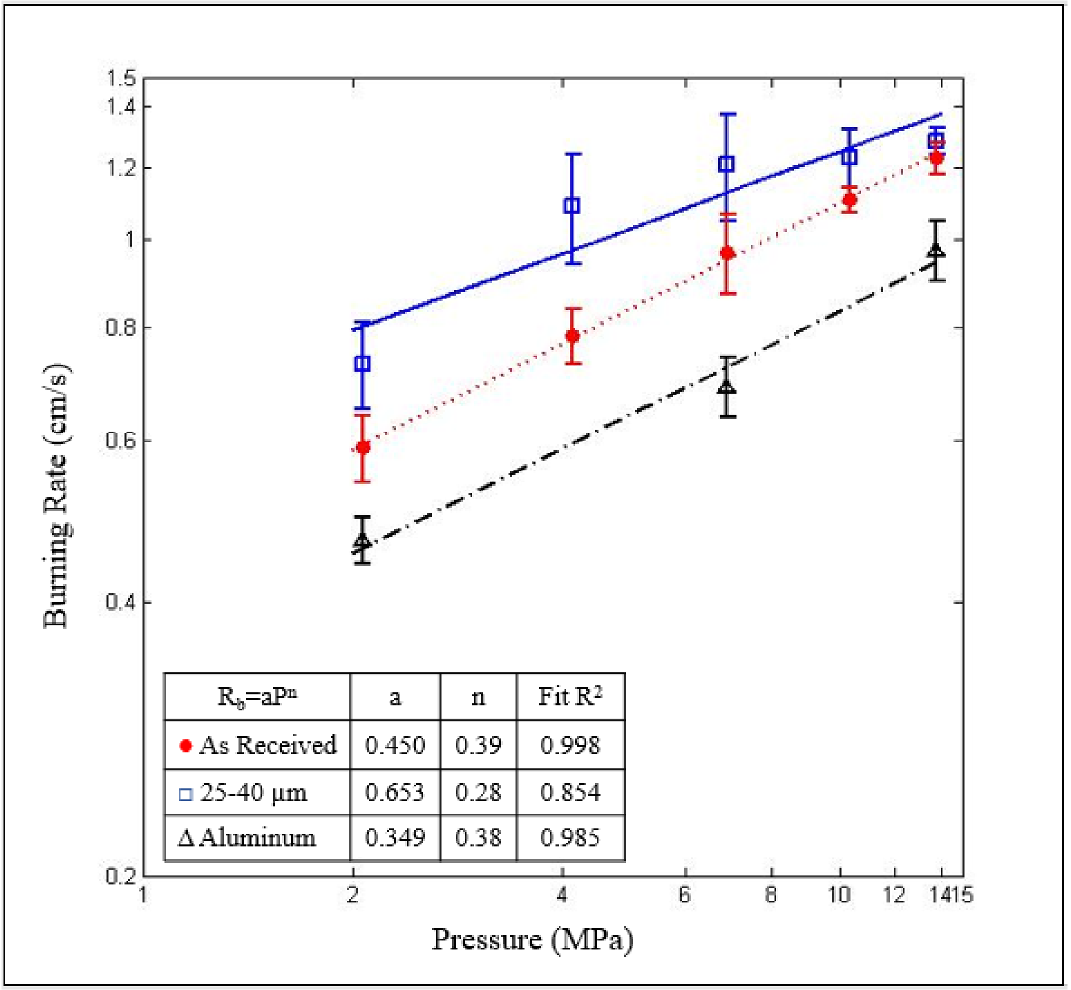


Figure 3.5 Side lit view of sieved aluminum-lithium (top) and neat aluminum (bottom) agglomerate products from a propellants burned at 6.89 MPa

locations within the droplet’s interior leading dispersive boiling of the lithium [5]. Therefore, the presence of microexplosions is dependent on droplet diameter. At higher pressures, the boiling point of lithium is increased, requiring a larger temperature for the core of the droplet to reach to ensure a microexplosion. Burning rate also increases at higher pressures, which means the droplet has less time to conduct heat and increase the core temperature. With both factors inhibiting microexplosions at high pressures, the larger agglomerate sizes at high pressures can be explained. The charted data for the agglomeration plots indicate that at high pressures the aluminum-lithium produced larger agglomerates than the aluminum. When the lighting on the disks was changed from bottom lit to side lit (Figure 3.5), it revealed that the aluminum disks consisted primarily of condensed phase oxide products (likely aluminum oxide). The aluminum-lithium, on the other hand, consisted of large molten metal droplets that did not combust prior to being quenched. These large molten droplets may have come from splashing emanating from the melt layer. If this is the case, then the possibility still exists that these metal droplets would still combust several centimeters above the burning surface, rather than the few millimeters at which the samples were collected. Condensed phase oxide products still appear on the quench disk, and their diameters do appear to be of comparable size to that of the neat aluminum propellant. Without a motor test, though, it is unclear whether the large liquid metal droplets would burn in the increased residence time provided by travelling the length of the port of a rocket motor or if significant two-phase flow losses will occur in the nozzle.

3.3 Burning Rate

The mean burning rate at several pressures and their power law curve fits are plotted in Figure 3.6. The pressure exponent of the as-received aluminum-lithium powder was measured to be 0.39 and the pressure exponent of the sieved powder was measured to be 0.28. Since the sieved powder was finer it displayed higher burning rates than the as-received aluminum-lithium at the full range of pressures tested. However, changing particle size typically does not effect the pressure exponent and in this instance the pressure exponent was about 0.11 less in the sieved material than in the as-received material [15]. As discussed previously, the sieved material produced smaller agglomerates at lower pressure than the as -received material. These smaller agglomerates may have been the result of increased microexplosivity. Additionally, higher pressures produced larger agglomerates due to a decrease in microexplosions. Therefore, with the pressure and fuel particle size dependence of microexplosions established by the particle collection data, it is reasonable to speculate that the increased microexplosivity of the sieved powder would somehow contribute to its increased pressure stability. However, further study would be needed to determine the exact mechanism through which this occurs. In spite of the particle collection data indicating the



$R_b = aP^n$	a	n	Fit R^2
● As Received	0.450	0.39	0.998
□ 25-40 μm	0.653	0.28	0.854
Δ Aluminum	0.349	0.38	0.985

Figure 3.6 Mean burning rates at various pressures

production of large unburnt metal droplets in the aluminum-lithium propellants, both burned at higher burning rates than the aluminum for all pressures tested. Additionally, the low pressure exponents of both aluminum-lithium composite propellants indicates that it is stable enough to be considered an acceptable candidate for use in a rocket motor.

CHAPTER 4. CONCLUSION

The combustion performance of a composite propellant using a one to one atomic aluminum-lithium alloy was demonstrated for the first time. Mixing difficulties were observed in environments with high absolute humidity (> 3500 ppmv), necessitating the use of a low-humidity environment for both mixing and curing. Particle capturing experiments demonstrated that droplet agglomeration is reduced due to the presence of shattering microexplosions. At higher pressure, though, these microexplosions may be inhibited by both the pressure and the increased propellant burning rate. Large, unburnt metal droplets were observed on the aluminum-lithium's quench disk samples, which may not have had enough time to combust in the short length scales used in this study. A scaled motor test would be needed to determine if these metal droplets create undesirably large two-phase flow losses. The burning rate was also measured and the pressure exponent was observed to be 0.29 for a propellant using aluminum-lithium powder sieved to 25-45 µm and 0.39 for aluminum lithium powder as received. The same formulation with aluminum fuel had a pressure exponent of 0.38. The decreased pressure exponent of the smaller particle aluminum-lithium propellant may have been the result of increased microexplosivity of the smaller powder size as indicated by the particle capturing data. Further study would be needed to identify precisely how the microexplosions would stabilize the propellant's pressure dependence.

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