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# Silicon alloying enhances fast heating rate combustion of aluminum particles



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### ABSTRACT

Alloys and composites of aluminum (Al) have shown promise in regulating and enhancing particle combustion for energy generation applications. Recent work on aluminum-silicon (Al-Si) spherical alloy particles has shown improved combustion at low heating rates through enhanced diffusion accompanying a lower melting temperature. This study extends reactivity analysis to higher heating rates, comparing oxidation of Al-Si with Al. Flame speeds of Al-Si powder mixed with molybdenum trioxide (MoO<sub>3</sub>) powder (Al-Si+MoO<sub>3</sub>) exhibited a faster transition to steady propagation relative to Al+MoO<sub>3</sub>. Bomb calorimetry experiments revealed up to 5.8% greater early temperature rise for Al-Si powder. Rapid steady propagation for Al-Si mixture and faster temperature rise for Al-Si particles were attributed to accelerated kinetics evidenced in thermal equilibrium analysis of the mixtures using a differential scanning calorimeter (DSC). Larger DSC exotherms in the early stages of oxidation (i.e., 480-720 °C) correlated with early heat release and promoted steady flame propagation for Al-Si+MoO<sub>3</sub> compared with Al+MoO<sub>3</sub>. Furthermore, in multiple heating rate DSC studies, Al-Si+MoO<sub>3</sub> ignited at a lower heating rate (i.e., 15 <sup>o</sup>C/min) than Al+MoO<sub>3</sub> (i.e., 20 <sup>0</sup>C/min). Both mixtures ignited at temperatures less than 625 °C which is above the melting temperature of Al-Si (574 °C) and below Al (659 °C). Thus, alloy particle fuels with enhanced diffusion-controlled kinetics promote steady flame propagation and show promise for energy generation applications. This is especially promising for technologies driven by enhanced condensed phase combustion such as some propellant additives or applications dependent on reliable burn rates such as pyrotechnic time delay formulations and primers.

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### 1. Introduction

Metal powders such as aluminum (Al) are well known for their use in energy generation applications due to high gravimetric (Al~31 kJ/g) and volumetric (Al~84 kJ/cm<sup>3</sup>) combustion energy [1,2]. Metal fuels are often an ingredient in propellants, explosives, and other pyrotechnics including thermite mixtures. Aluminumbased mixtures also have potential applications for welding, combustion synthesis of ceramics and composites, and as gas generating agents for automobile airbags [3–5]. Improved burning rates would enhance the performance of Al for these applications. Other applications such as ignition delay compositions necessitate precise time delay control between two ignition events with high repeatability and reliability [6]. Thus, controlled burning rates of aluminum powders are an important area of research towards their improved application performance.

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An important characteristic of an Al powder mixture is a steady predictable flame speed [7]. Flame speed is the rate of selfpropagation of the exothermic reaction that, upon ignition, proceeds through the reactant mixture in a layer-by-layer fashion and is influenced by physical and chemical properties of the mixture. Because flame speed is dependent upon self-sustained flame propagation, energy propagated by the reaction must exceed energy losses. Particle size & composition, mixture composition & homogeneity, and inclusion of additives are all important considerations that influence flame speed [3]. For example, in Ilunga et al. [8], a silicon-bismuth oxide (Si-Bi<sub>2</sub>O<sub>3</sub>) additive was used to regulate the ignition and subsequent propagation of aluminum-copper oxide (Al-CuO) thermite. Lowered ignition thresholds promote ignition of reactants by the heat released from combustion thereby promoting flame propagation. They found that the concomitant energy release provided by Si-Bi<sub>2</sub>O<sub>3</sub> helped kick-start the Al-CuO reaction allowing it to ignite faster than Al-CuO alone. Additionally, the Al-CuO+Si-Bi<sub>2</sub>O<sub>3</sub> mixture self-propagated faster than Si-Bi<sub>2</sub>O<sub>3</sub> alone.

New pyrotechnic compositions also show promise in terms of lowered toxicity. As noted in 2004 by Giles [9], a survey [10] found

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that employees who had just cleaned a firing range "had levels of lead in their blood almost ten times as high as US government health limits". Thus alternative, yet reliable primer formulation development for ballistic applications is needed. Giles [9] reported on nanoparticles of aluminum combined with acetylene black and molybdenum trioxide (MoO<sub>3</sub>) as an alternative to leadazide and lead-styphnate in primer formulations. The nanoparticles are ignition-sensitive promoting ignition in a layer-by-layer fashion to reliably produce self-propagation of the reaction and thus are an alternative to lead-based formulations.

Apart from mixture composition, the size of the fuel particle influences reactivity. Micron-sized aluminum particle fuels are not as easy to ignite as their nanoparticle counterpart, and often result in slow flame speeds and incomplete combustion [11]. Additionally, nano-sized particles can facilitate processing for synthesis applications due to characteristics such as improved sintering properties [12]. For micron-sized aluminum, manipulating mixture formulation chemistry as demonstrated by Ilunga et al. [8] could have tremendous benefits toward not only enhancing ignition sensitivity but also promoting steady self-propagation.

The phase of combusting material can also have an impact on its combustion performance. For example, Ishihara and Brewster showed that condensed phase combustion for boron (B) and magnesium (Mg) additives drives increased propellant burning rate as compared with aluminum additives [13]. Thus, increases in condensed phase combustion through engineering modifications to the particle could increase burning rate for aluminum additives as well.

Enhanced reactivity of the fuel particle alone can also influence mixture performance. In this context, recent studies have shown that alloys, mixtures, and composite fuel particles can regulate particle combustion thereby delivering improved efficiency, increased flame speed, and lowered ignition energy and temperature [14-16]. Combinations of metalloids have recently been introduced to exploit attributes of separate materials. For example, silicon (Si) has shown potential for catalyzing reactions when combined with boron (B) thereby creating active sites on boron. Chen et al. [17] used a laser pyrolysis synthesis method to produce particles ranging from 15 to 42 atomic% B combined with Si and the particles were stable up to an annealing temperature of 600 °C. The B-Si particles showed lower apparent activation energy and significantly higher reaction rates (at least three times greater) at 450 °C compared with other boron-based catalysts such as porous boron nitride and hexagonal boron nitride. Nano-aluminum (nAl) has also been used to enhance combustion properties of B that has formed a non-reactive surface oxidation layer due to long-term exposure to air after storage for 10 years [18]. The B particles were coated with nAl using wet ball-milling methods that distributed nAl on the B surface. The nAl-coated B particles increased burning rates by 2.4-3.4 times that of stored B.

Recent work by Vaz et al. [16] examined Al-Si alloy particles in a simultaneous differential scanning calorimeter (DSC) thermogravimetric analyzer (TGA) under oxygen-rich conditions. Al-Si particles demonstrated improved combustion relative to Al particles with similar shape and size distribution. The lower melting temperature of the Al-Si binary eutectic (574 °C) compared to Al (659 °C) enhanced Al-Si particle diffusion rates resulting in more complete combustion of Al-Si at lower temperatures than Al particles. The study by Vaz et al. [16] introduced the potential to use Al-Si in place of Al particles in non-equilibrium reactions for improved energy generation and heat transfer.

The goal of this study was to extend work by Vaz et al. [16] and examine the combustion of Al-Si alloy particles at higher heating rates corresponding to non-equilibrium, thermal runaway reaction conditions. Firstly, flame speed experiments were performed in an open flow system and incorporated a solid oxidizer, molybdenum trioxide (MoO<sub>3</sub>) powder, that was individually mixed with the Al and Al-Si powders. Additionally, closed system bomb calorimetry measurements of heat of combustion and rate of temperature rise were conducted for Al and Al-Si powders. A mechanistic understanding of the non-equilibrium fuel particle combustion required further analysis of exothermic behavior in thermal equilibrium studies of Al+MoO<sub>3</sub> and Al-Si+MoO<sub>3</sub> using DSC and TGA measurements.

Results from this study address the fundamentals of flame propagation and have implications toward systems containing reactive particulate solids. Key applications optimized by steady, selfsustained burning rates include ignition delay and primer formulations that benefit from precise control of a self-propagating reaction or in propellant systems that benefit from condensed phase heat release that can increase propellant burning rates.

### 2. Materials and methods

### 2.1. Materials

Aluminum (nominal size 1–2  $\mu$ m diameter, Product Number 0230HJ) and Al-Si (nominal size 1–2  $\mu$ m diameter, Product Number 0271DX) powders were obtained from Skyspring Nanomaterials (Houston TX, USA). The characterization of these materials, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA) and particle size distribution have been previously reported [16]. Both Al and Al-Si particles were spherical in shape and their size distributions were similar. Physical similarities were important selection criteria in this study's design to mitigate variations in burning behavior that may be a function of particle size and morphology. The key variable of interest was the compositional difference between the two fuel particles. The XRD patterns showed a 100 wt.% Al composition for the Al powder and a 92.7 wt.% Al and 7.3 wt.% Si composition for the Al-Si powder. The melting point of the Al-Si powder is 574 °C which corresponds with a eutectic composition [16,19,20]. The difference between melting point and compositional analysis is likely attributable to dissolution of some Si in Al [21] and tolerances in the XRD measurements. The melting temperature of Al-Si is 85 °C less than Al at 659 °C [16,22].

Molybdenum trioxide,  $(MoO_3)$  powder with nominal particle size 100 nm (Product Number 3851XW) was procured from Nanostructured and Amorphous Materials Inc. (Katy, TX, USA). An XRD analysis confirmed 100 wt.% MoO<sub>3</sub>. Wang [3] described MoO<sub>3</sub> as chemically stable but physically unstable because it sublimes when heated. Blackburn et al. [23] calculated Gibbs Free energy of MoO<sub>3</sub> and showed sublimation starts at ~530 °C, very slowly at first and later the majority of sublimation occurred from ~720 °C upwards. In this study MoO<sub>3</sub> was selected because it is a commonly used oxidizer in pyrotechnic and thermite applications [3,9].

### 2.2. Mixture preparation

Fuel-oxidizer powder mixtures of Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub> were prepared in batches of upto 3500 mg and followed the same mixing procedure for flame speed and DSC/TGA experiments. Chemical equilibrium software (i.e., NASA CEA [24,25]) was used to calculate adiabatic flame temperatures of fuel-oxidizer mixtures to examine the effect of Si inclusion with Al and identify an equivalence ratio resulting in the highest flame temperature that would be optimum for the experiments. Calculations were performed for Al-Si + oxygen (O<sub>2</sub>), Al+O<sub>2</sub>, Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub>. These mixtures were analyzed for a range of equivalence ratios ( $\Phi$ ) from 0.7 to 1.3 based on combustion of XRD-determined compositions of the reactant powders. Flame temperatures were calculated for an

open system under conditions of constant enthalpy and constant atmospheric pressure with reactants starting near room temperature ( $\sim 28$  <sup>0</sup>C) [24,25].

Based on these calculations, an equivalence ratio of 1.1 corresponds to a peak adiabatic flame temperature of  $3422 \ ^{0}$ C for Al-Si+MoO<sub>3</sub> and was the designated mixture ratio for DSC/TGA and flame speed experiments. Mixture preparation was performed similar to methods described in [26]. Fuel (Al or Al-Si) powder was mixed with MoO<sub>3</sub> powder in a sample cup containing approximately 100 ml of isopropanol and up to 3500 mg of powder mixture. The isopropanol carrier fluid facilitates improved mixing using ultrasonic waves from a Sonicator 3000 (Misonix, Inc). Ultrasonication was programmed for 10 min in a 10 s on-off cycle to avoid sample heating. The slurry was poured into a ceramic dish so that the carrier fluid could evaporate over a duration of approximately 24 h. Then, the powder mixture was reclaimed through a 325 mesh to avoid agglomeration prior to further testing.

### 2.3. Flame speed measurement

Flame speeds for Al-Si+MoO3 and Al+MoO3 were measured in duplicate using a flame tube apparatus previously described in [26–28]. The flame tube confines flame propagation to the axial direction. The tube was made of transparent guartz with 10 cm length, 3 mm inner diameter, and 8 mm outer diameter. Each tube was filled with 544 mg of powder mixture with a quarter inch left vacant at one end of the tube to accommodate a nichrome ignition wire that was secured in place with insulation tape. All tubes were filled to a bulk density of 20% of their theoretical maximum density (TMD) i.e., a loose powder-filled tube. Upon ignition, the video data was captured with a Phantom v 2512 high speed camera with a Nikon Sigma 24-70 mm, 1:2.8 ExDG lens fitted with an 82 mm Tiffen variable neutral density filter set to maximum. The aperture of the camera was set to 32 f-stop. The camera used an exposure time of 1 µs with a frame rate of 80,000 fps and an image resolution of 896×112 pixels. Flame front tracking was analyzed with the Phantom Camera Control (PCC) software with image sensitivity enhanced while tracking the flame front. The flame tube was secured in a holder that obscured the ends of the tube so approximately 7.5 cm of the tube was measured during flame front tracking. In the plot of flame front position versus time, steady state propagation was considered to be achieved when the regression coefficient  $(R^2)$  of the straight-line fit reached 0.995 or greater.

### 2.4. Parr bomb calorimeter

A Parr 6400 Automatic Isoperibol Calorimeter (Parr Instrument Co.) was used to measure the heat of combustion and rate of temperature rise associated with the combustion of Al and Al-Si powders. These experiments were only performed for the fuel powders purposefully to assess how fuel oxidation differences under nonequilibrium conditions may influence flame propagation within the mixture. This is especially pertinent since DSC/TGA results indicate that early exotherms for Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub> may be a function of fuel oxidation alone without much participation of MoO<sub>3</sub> (See Section 3.2). Experiments were performed by dispersing the powder in a porous medium i.e. a starch-based packing peanut (The Office Depot Product # 578-376 [29]) and ignited in a boron nitride (BN) ceramic crucible inside a 1138 Oxygen Combustion Vessel (Parr Instrument Co.) with pressurized oxygen at 30 atmospheres [30]. This experimental design allows for a simulation of suspended particle burning to quantify total heat of combustion and extract information about the transient thermal heating associated with fuel powder combustion. Each experiment used approximately 0.051 g of metal powder (either Al or Al-Si) combined with approximately 0.11 g of dispersing medium. The heat generated in this process was transferred through the wall of the combustion vessel and to a surrounding bucket containing water. The rate of water temperature increase was analyzed to infer the rate of heat release associated with the combusting powder.

## 2.5. Differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA)

Thermal equilibrium analysis of both mixtures was conducted in a NETZSCH STA 449 F3 Jupiter DSC/TGA machine. Temperature and sensitivity calibrations of the DSC were conducted with calibration materials including indium, tin, bismuth, zinc, aluminum, silver, and gold. Melting temperatures were within 1 <sup>o</sup>C of standard reference values. Enthalpies measured with sensitivity calibration were within 1.1% of standard reference values for In and Au up to 15 <sup>o</sup>C/min and within 5% for 20 <sup>o</sup>C /min heating rates. The TGA mass calibration was done using calcium oxalate and was within 1% of standard reference values.

All DSC/TGA experiments used approximately 10 mg powder samples in open alumina crucibles and an environment of 80% Ar and 20%  $O_2$  by volume to approximate the  $O_2$  concentration of air. Also, all experiments were performed for a temperature range of 25–1200 °C. Experiments performed on the mixtures at 10 °C/min heating rate were conducted in triplicate to confirm reproducibility. An additional experiment was performed for MoO<sub>3</sub> alone at 10 °C/min heating rate to measure the rate of sublimation. Also, experiments were performed for mixtures at multiple heating rates to quantify apparent activation energy. For the latter series of experiments, heating rates of 5, 7, 15 °C/min were programmed for both mixtures and additionally 20 °C/min for Al+MoO<sub>3</sub>. All measurements from analysis of the data were expressed in terms of initial sample mass.

### 3. Results and discussion

### 3.1. Flame speed measurements

Fig. 1 shows a representative single replicate of flame speed determined by analyzing the flame front position as a function of time. Fig. 1a shows unsteady propagation for Al+MoO<sub>3</sub> with an unsteady region that occurs over the initial ~10% of the length for a duration on the order of 0.1 ms. Unsteady propagation is not seen for Al-Si+MoO<sub>3</sub> in Fig. 1b. Over duplicate measurements, the eventual steady state propagation for both mixtures is similar. Speeds are in the range of 162–175 m/s for both mixtures with averages of 168.3  $\pm$  3.7 m/s for Al-Si+MoO<sub>3</sub> and 168.42  $\pm$  8.7 m/s for Al+MoO<sub>3</sub> (excluding unsteady behavior) - indicative that convective energy transport is dominant and consistent with gas generating properties of MoO<sub>3</sub>. The absence of Si in Al particles affects early stages of combustion but the burning rate for both mixtures is similar once steady propagation is achieved.

### 3.2. Bomb calorimetry measurements

Bomb calorimetry measurements reveal similar heat of combustion for both powders. The heat of combustion of Al-Si is 30,523 J/g and Al is 30,087 J/g, within 2% and 3.1% respectively, of the theoretical values of combustion of XRD-determined reactant compositions [31]. The differences in measured heat of combustion are within 1.4% of each other and within the uncertainty of the measurement technique [30]. Thus, the addition of Si to Al does not significantly alter the potential chemical energy stored within the fuel particle.

Results of NASA CEA calculations comparing the thermodynamics of Al-Si and Al oxidation are shown in Fig. 2. The addition



**Fig. 1.** Flame front position versus time and straight-line curve fits for flame speeds. A steady flame speed calculated from straight line fit of  $R^2$  of at least 0.995. (a) Al+MoO<sub>3</sub> average flame speed linear fit  $R^2 = 0.9875$ , steady flame speed linear fit  $R^2 = 0.9951$ . (b) Al-Si+MoO<sub>3</sub> average steady flame speed linear fit  $R^2 = 0.9952$ . All flame speeds are rounded to the nearest integer.



Fig. 2. NASA CEA calculation of adiabatic flame temperature for combustion of Al and Al-Si in (a) oxygen (O<sub>2</sub>), and (b) molybdenum trioxide (MoO<sub>3</sub>) with conditions of constant enthalpy and constant pressure of 1 atmosphere.

of Si does not appreciably change the flame temperature in either case for combustion with oxygen or combustion with MoO<sub>3</sub>. The maximum difference in the former case is 23 <sup>0</sup>C or 0.59% of the Al flame temperature at an equivalence ratio,  $\Phi = 0.7$  and in the latter case is 296 <sup>0</sup>C or 8.52% of the Al flame temperature at  $\Phi = 0.8$ . The maximum flame temperature for Al-Si+MoO<sub>3</sub> occurs at  $\Phi = 1.1$  and is 74 <sup>0</sup>C or 1.98% lower than the Al+MoO<sub>3</sub> flame temperature. Relatively small variations in flame temperature are not surprising, given that the heat of combustion of Si ( $\sim$ 32 kJ/g) is similar to that for Al ( $\sim$ 31kJ/g). Similar heat of combustion and flame temperature suggest that the heat capacity of resulting combustion products does not vary appreciably for Al and Al-Si. Thus, any improvement in combustion behavior of Al-Si is not likely due to these thermodynamic properties of the mixtures, but instead accelerated diffusion rates promoted by differences in melting temperature of the fuel powders.

Another observation from Fig. 2 is that at higher equivalence ratios, the MoO<sub>3</sub> reaction temperatures approach each other. A reduced Mo product concentration for high (fuel rich) equivalence ratios brings the two MoO<sub>3</sub>-based reactions thermodynamically in closer range. Also, silicon combustion results in silicon oxides (i.e., quartz) that have a lower boiling point than aluminum oxides. Overall, silicon oxides will dissociate into gaseous species render-

ing silicon oxidation less exothermic than aluminum oxidation under equilibrium conditions.

Data from the bomb calorimeter can also be used to measure the rate of temperature rise resulting from the reaction heat that is transported through the calorimeter wall, and into the water bath bucket. Fig. 3(a) shows the change in normalized temperature of water ( $\Delta T_N$ ) defined in Eq. (1).

$$\Delta T_N = (T(t) - T_{min}) / (T_{max} - T_{min})$$
<sup>(1)</sup>

In Eq. (1), T(t) is the temperature at the corresponding time t,  $T_{min}$  is the minimum or starting temperature at the beginning of ignition and  $T_{max}$  is the maximum or end temperature. The ratio of normalized water temperature for both powders is shown in Fig. 3(b) as a function of time. There is a 5.8% increase in temperature rise associated with the Al-Si powder. A faster temperature rise at early times is qualitatively suggestive of greater radiant heat exchange associated with the combustion process for Al-Si. Radiant exchange will be faster than conductive or convective modes of heat exchange in the bomb calorimetry experiment. The faster rise in temperature associated with Al-Si powder is also consistent with the observations in Fig. 1 for more rapid steady state propagation of the Al-Si powder. Both experiments indicate that the heat



**Fig. 3.** (a) Comparison of normalized bomb calorimeter water bucket temperatures for Al (solid line) and Al-Si (dashed line) after the point of ignition which occurs at t = 220 s after initiation of experiment (b) Ratio of normalized water bucket temperatures for Al-Si: Al showing Al-Si exhibits faster temperature rise.

transfer processes are greater at early times for Al-Si powder relative to Al powders.

### 3.2. Thermal equilibrium measurements

Results of averaged curves from DSC and TGA triplicate measurements at 10  $^{0}$ C/min heating rate in an 80:20 Ar:O<sub>2</sub> by volume environment are shown in Fig. 4. The replicates measured from the same mixing batch are independent and show heterogeneities, especially in the higher temperature exotherms.

Low temperature exotherms, shown in Fig. 4a, up to  $\sim$ 720 <sup>0</sup>C are greater for Al-Si+MoO<sub>3</sub> totaling 1318 J/g compared to 1070 J/g for Al+MoO<sub>3</sub>. The standard deviations of the early exothermic enthalpy for Al+MoO<sub>3</sub> and Al-Si+MoO<sub>3</sub> are 10 J/g and 68 J/g, respectively. The *p*-value between Al+MoO<sub>3</sub> and Al-Si+MoO<sub>3</sub> for this early enthalpy is less than 0.02 (two-tailed Welch t-test [32]), indicating a measurable and distinct difference. Low temperature exotherms show promise for enhancing condensed phase heat release that correlate with improved propellant burning rates [13].

The corresponding mass increase is shown in the TGA measurements in Fig. 4b. The low temperature exotherms result in a net mass gain despite the majority of the mixture consisting of  $MoO_3$  which is only likely to lose mass through sublimation at more elevated temperatures [23,33] and seen here to accelerate at 720 °C or greater (See Fig. 4c and its description below). Thus, the low temperature exotherms result from oxidation with oxygen gas in the DSC atmosphere and not with sublimated  $MoO_3$ . A slightly higher average mass gain occurs at lower temperatures for Al-Si compared with Al, indicating accelerated diffusion-controlled kinetics through the particle shell for Al-Si, previously seen in [16]. Differences in thermal equilibrium behavior may correlate to variations in steady flame propagation with Al-Si+MoO<sub>3</sub> showing greater early-stage oxidation consistent with rapid steady flame propagation.

Higher temperature exotherms (i.e., > ~720 <sup>0</sup>C) are 2474 J/g for Al+MoO<sub>3</sub> compared to 2144 J/g for Al-Si+MoO<sub>3</sub>, although this difference is not statistically significant (p > 0.05, two-tailed Student's t-test [32]). The standard deviations for Al+MoO<sub>3</sub> and Al-Si+MoO<sub>3</sub> are 183 J/g and 306 J/g, respectively. Therefore, while there are measurable differences in early-stage reaction kinetics, later-stage reaction kinetics are similar. Heterogeneities in the later stage exotherms likely arise from differences in the dynamics of the low temperature exotherms and heterogeneities in the mixing process.

The later stage exotherms in Fig. 4b overlap with an initial mass gain of approximately 5–7% followed by a drop in mass of 37–38%,

corresponding with sublimation of MoO<sub>3</sub> as shown in Fig. 4c. A TGA analysis of MoO<sub>3</sub> in Fig. 4c shows that the majority of sublimation and concurrent mass loss occur between 627 °C and 963 °C corresponding to 83% of the initial mass. Though MoO<sub>3</sub> mass loss begins at 627 °C, only 0.84% mass loss occurs between 627 °C and 720 °C. Therefore, the majority of MoO<sub>3</sub> sublimation overlaps with the second exotherm in Fig. 4b and net mass loss of ~31–33%. Fig. 4c corresponds well with the literature which states that MoO<sub>3</sub> sublimation begins very slowly at ~530 °C [23], with only < 0.01% occurring at this temperature, and most sublimation occurring after 720 °C. Condensation of sublimated MoO<sub>3</sub> can cause mass gain [34], thus the lack of complete mass loss for MoO<sub>3</sub>. This data can be used to infer the following reasoning and conclusions about the mechanisms of heat release under thermal equilibrium conditions.

The MoO<sub>3</sub> is approximately 71 wt.% of the initial mixture. In the DSC/TGA data interpretation, there are two assumptions. The first is that mass gain corresponding to the first exotherm (i.e.,  $\sim 8\%$ ) is due to fuel oxidation from atmospheric O<sub>2</sub>, and no MoO<sub>3</sub> sublimation occurs during the first exotherm. The second is 83% of MoO<sub>3</sub> is sublimated during the second exotherm. Given these assumptions, during the second exotherm the fuel would have to gain roughly 26-28 wt.% to account for net mass loss of  ${\sim}31\text{--}33\%$ . The 26-28% mass gain during the second exotherm results in a total mass gain of 35-36%. The 35-36% mass gain compares favorably with the expected mass gain for complete conversion to Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> which would be  $\sim$ 26%. The difference between the expected mass gain ( $\sim$ 26%) and experimental mass gain ( $\sim$ 36%) may be attributed to increased condensation of sublimated MoO<sub>3</sub>. Other interactions may also occur such that some MoO<sub>3</sub> sublimation may occur during the end of the first exotherm. However, small deviations in stages of fuel mass gain are unlikely to affect the main conclusion: Al-Si oxidizes earlier due to enhanced diffusion through the particle shell that enhances heating rate and influences more rapid steady-state flame propagation.

Since the increased enthalpy of low temperature exotherms of Al-Si+MoO<sub>3</sub> are statistically significant, multiple heating rates were analyzed to measure activation energy. The results are shown in Fig. 5(a) and (b). Two observations are noteworthy. First, Al-Si+MoO<sub>3</sub> ignites at a lower heating rate (15  $^{\circ}$ C/min) than Al+MoO<sub>3</sub> (20  $^{\circ}$ C/min). Second, both mixtures ignite at temperatures less than 625  $^{\circ}$ C, which is above the Al-Si melting temperature of 574  $^{\circ}$ C and below the Al melting temperature of 659  $^{\circ}$ C. Therefore, higher early-stage enthalpy and ignition at a lower heating rate are evidence of accelerated diffusion attributed to phase change associated with the lower melting temperature of Al-Si powder.



**Fig. 4.** (a) Heat flow as a function of temperature for Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub> in an atmosphere of 80% Ar:20% O<sub>2</sub> by volume with a heating rate of 10 °C/min. Note the larger early exotherms for the Al-Si+MoO<sub>3</sub> average of 1318 J/g vs 1070 J/g for Al+MoO<sub>3</sub> (p < 0.02, two-tailed Welch t-test). (b) Corresponding TGA mass change data. (c) TGA mass change data for MoO<sub>3</sub> alone heated under the same environment- 80% Ar:20% O<sub>2</sub> by volume. and heating rate - 10°C/min - as the thermite mixtures. All enthalpy measurements are rounded to the nearest whole number. TGA mass change measurements are rounded to the first decimal place. All onsets correspond to the beginning of the exotherm or mass gain as defined in UNE-EN ISO 11357-1 [35].

An activation energy analysis for both stages of exotherms was conducted using the Kissinger method [36-38] using Eq. (2) and data from Fig. 5.

$$\ln\left(\beta/T_p^2\right) = c - E_a/RT_p \tag{2}$$

In Eq. (2),  $\beta$  is the heating rate,  $T_p$  is the peak absolute temperature of the exotherm,  $E_a$  is the apparent activation energy, R is the universal gas constant and c is a constant.

For the first exothermic peak, non-linearities exist in the activation energy plot based on Eq. (2). These non-linearities are likely due to multiple overlapping processes occurring during the early oxidation stage (i.e., < 720 <sup>o</sup>C) including melting of Al-Si and Al, oxidation of Al-Si and Al and possible interactions with MoO<sub>3</sub>. The latter includes MoO<sub>3</sub> sublimation or MoO<sub>3</sub> in the solid phase acting as a heat sink due to its heat capacity relative to the metal. However, since no corresponding net mass loss is observed in the TGA data, it is likely MoO<sub>3</sub> remains mostly in the solid phase throughout early-stage oxidation.

For the second exothermic peak, Al+MoO<sub>3</sub> has an activation energy of 127 kJ/mol. The Al+MoO<sub>3</sub> activation energy is non-linear whereas Al-Si+MoO<sub>3</sub> has an almost linear trend with a regression coefficient of  $R^2 = 0.9813$ . The linearity provides one piece of evidence that the heat released in the second exothermic peak of Al-Si+MoO<sub>3</sub> is controlled by a single process i.e., Al-Si oxidation.

For Al-Si+MoO<sub>3</sub>, the activation energy of 135 kJ/mol is close to the Kissinger method value for oxidation of Al and Al-Si particles in an oxygen-rich environment [16], i.e., 138.8 kJ/mol. The good agreement between activation energies implies that the mechanism of oxidation is likely similar in the case of MoO<sub>3</sub> and O<sub>2</sub>, i.e., diffusion of fuel/oxygen through the shell and oxidation at the exterior of the fuel particle. It is also possible that MoO<sub>3</sub> sublimation might contribute to an oxygen-rich environment in the vicinity of the Al-Si particle thus bringing its environment closer to the 80% level in the previous study [16]. The oxygen content around the particle may be at an intermediate saturation level, i.e., between 20 and 80 vol.% and ensures oxidation similar to measurements by Vaz et al. [16].

The non-linearity seen in the Al+MoO<sub>3</sub> activation energy graph for the later exothermic peak is likely due to overlapping processes that include stages of MoO<sub>3</sub> sublimation and Al oxidation. Since non-linearity was also seen for oxidation of Al particles in 80% O<sub>2</sub> environment [16], at least some of this non-linearity originates from the Al particle itself.

### 4. Discussion

A conceptual model is developed based on activation energy and used to illustrate the trends of lowered threshold temperature



**Fig. 5.** Heat flow for multiple heating rates in 80:20 Ar: $O_2$  by volume for (a) Al+MoO<sub>3</sub>, note: 20°C/min curve is truncated in the region of ignition. (b) Al-Si+MoO<sub>3</sub>, note: 15 °C/min curve is truncated in the region of ignition. Approximate regions of exothermic peak 1 and peak 2 used in activation energy calculations are indicated. (c) Activation energy for Al-Si+MoO<sub>3</sub> based on Eq. (2) and exothermic peak 2 in (b). R<sup>2</sup> value for straight-line fit of activation energy graph is 0.9813 for Al-Si+MoO<sub>3</sub>. Activation energy graphs based on exothermic peak 1 for both mixtures and peak 2 for Al+MoO<sub>3</sub> are non-linear and hence not shown.



**Fig. 6.** Comparison of ignition thresholds for Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub> based on heat release due to combustion (solid line = Al+MoO<sub>3</sub>, dashed and dotted line = Al-Si+MoO<sub>3</sub>) and heat loss due to conduction (dashed line = Al+MoO<sub>3</sub>, dotted line = Al-Si+MoO<sub>3</sub>).

and energy for ignition and consequent steady self-propagation seen in  $Al-Si+MoO_3$ . Fig. 6 shows a concept sketch illustrating points of ignition for both powders. Ignition is defined to occur at the intersection of heat gain due to liberated chemical energy and heat loss due to conduction away from the mixture to the surrounding atmosphere [39]. Heat gain and heat loss are estimated by Eqs. (3) and (4), respectively [39]. It is noted that the equation for heat gain (Eq. (3)) assumes that the order of reaction is the same for both mixtures and reaction order does not change in the initial stages of the reaction.

$$Q_{gain} = k \cdot \Delta H_r$$
, where  $k = A \exp(-E_a/RT)$  (3)

$$Q_{loss} = C(T - T_a) \tag{4}$$

In Eq. (3),  $Q_{gain}$  is the rate of heat gain, and  $\Delta H_r$  is the overall heat of reaction assumed to be the same for both Al+MoO<sub>3</sub> and Al-Si+MoO<sub>3</sub> and equivalent to 465 kJ/mol i.e. heat released due to complete combustion of 1 mole of Al when combined with MoO<sub>3</sub>. The rate constant k is dependent on Arrhenius pre-exponent A, activation energy  $E_a$ , Universal Gas Constant R, and absolute temperature T. Arbitrary values are chosen for  $A = 10^{11}$  for both mixtures, and  $E_a = 150 \text{ kJ/mol}$  for Al+MoO<sub>3</sub> and 135 kJ/mol for Al-Si+MoO<sub>3</sub> such that  $E_a$  for Al-Si+MoO<sub>3</sub> is 90% of  $E_a$  for Al+MoO<sub>3</sub>. In Eq. (4),  $Q_{loss}$  is the rate of heat loss due to conduction of heat away from the mixture and towards the surrounding atmosphere. This is dependent on the temperature of the mixture T, ambient temperature  $T_a$  and C is a coefficient derived from the geometry and thermal properties of the sample and equal to thermal conductivity of Al and Al-Si for this calculation. T<sub>a</sub> is 298.15 K and C is 213 W/mK for Al and 155 W/mK for Al-Si [40]. The values for C associated with the fuel are considered indicative of the mixture for the purposes of comparing their relative ignition temperatures. The resulting plots are illustrated for temperature in °C to enable comparison with other graphs.

The estimated resulting threshold temperature for steady selfpropagation of Al-Si+MoO<sub>3</sub> is 113 <sup>o</sup>C lower than Al+MoO<sub>3</sub>. Assuming a heating rate of 10<sup>7</sup> K/s upon ignition (i.e., one order of magnitude lower than ~10<sup>3</sup> m/s flame speed for Al nanoparticle thermites [27]) the reduced threshold temperature would result in an ignition time difference of 0.01 ms between Al-Si+MoO<sub>3</sub> and Al+MoO<sub>3</sub> for subsequent ignition of unburnt mixture. Given that the time for achievement of steady propagation in Al+MoO<sub>3</sub> is one order of magnitude higher than ignition delay, several such ignition events must occur before steady propagation is achieved in Al+MoO<sub>3</sub>. The conceptual graphic in Fig. 6 exemplifies the differences in reaction properties that result in more rapid steady propagation associated with the Al-Si particles.

After ignition, the magnitude of flame speed suggests that the flame is mostly convectively driven by gasified  $MoO_3$  with a radiant energy contribution as evidenced by the bomb calorimetry results. Flame speed results indicate that eventually heat gained by oxidation significantly exceeds losses and sustains steady propagation of both mixtures, but early-stage kinetics help promote steady propagation for Al-Si owing to diffusion enhanced by a lower melting temperature.

### 5. Conclusions

The combustion of spherical Al and Al-Si particles of similar size distribution, when combined with a solid oxidizer powder,  $MoO_3$ , was investigated. The two thermites were experimentally investigated for flame speed measurements using visual data from propagating reactions in a flame tube, and the fuel powders were also examined for heat of combustion measurements in a bomb calorimeter. Further examination of the reaction kinetics for both thermites was performed using differential scanning calorimetry (DSC)/ thermogravimetric analysis (TGA) thermal analysis techniques. In all cases, early stages of combustion were clearly accelerated in Al-Si powder compared with Al powder.

While steady flame speeds were similar (162-175 m/s), distinct differences between the two fuels in propagation behavior up to steady propagation were interestingly repeatable. The Al+MoO<sub>3</sub> exhibited unsteady propagation up to a  $\sim$ 10% entry length preceding steady propagation whereas Al-Si+MoO<sub>3</sub> exhibited steady propagation almost instantaneously. Experiments using a bomb calorimeter showed similar heats of combustion for Al of 30,087 J/g and Al-Si of 30,523 J/g. While the global measurements are similar, the two fuel powders exhibited differences in rates of temperature rise. Specifically, Al-Si exhibited a 5.8% greater early increase in the normalized temperature within the calorimeter compared with Al, which is an indication of stronger radiant energy transport for Al-Si powder combustion. The increased early temperature rise is consistent with a more rapid transition to steady flame propagation. Equilibrium kinetics also revealed significant differences in the magnitude of low temperature exothermic energy release from the two mixtures. The Al-Si+MoO<sub>3</sub> mixture showed larger early exothermic energy and ignition at a lower heating rate than Al+MoO<sub>3</sub>. The thermal equilibrium results provide evidence for faster diffusion-controlled kinetics for Al-Si owing to its lower melting temperature resulting in increased condensed phase combustion.

A conceptual model was developed integrating the above results to describe the influence of energy gain and loss in establishing a steady self-propagating reaction. An analysis of threshold temperature for ignition revealed a 113 °C reduction for Al-Si relative to Al particles, which has impact on propagation through the unreacted mixture. Such a lowered temperature threshold would lead to Al-Si+MoO<sub>3</sub> having an ignition delay on the order of 0.01 ms shorter than Al+MoO<sub>3</sub> at high heating rates. Therefore, several such ignition events must occur before the Al thermite flame speed catches up with Al-Si+MoO<sub>3</sub>, thus explaining the experimental results.

All of these results show that Al-Si powders demonstrate more rapid diffusion-controlled oxidation kinetics, increased condensed phase combustion, increased radiant heat transfer and promote early heat release for rapid transition to steady flame propagation compared with Al powders. These results for Al-Si fuel particles have implications for improved propellant burning, thermite welding, combustion synthesis, gas generation, steady burning fuses, pyrotechnic time-delay, and primer technologies. Most interesting to note is the potential for improved condensed-phase combustion to increase propellant burning rate and steady flame propagation to properly control fuse/primer/time delay burning rate.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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