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Thermite reactivity with ball milled aluminum-zirconium fuel particles

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ABSTRACT

Thermite reactivity is a function of the reactant particle size. However, metallurgical strategies that purposefully engineer larger fuel particles to be as reactive as their smaller scale counterparts could be a transformative development in thermite combustion. In this study, ball milled aluminum/zirconium (Al:Zr) particles are prepared with four different Al:Zr particle size ranges (0-10, 10-32, 32-53 and 53-75 µm) and similar internal microstructures to understand the influence of particle size on reactivity within thermite mixtures. The thermites are prepared by combining the Al:Zr particles with molybdenum trioxide (MoO₃) particles and reactivity was assessed using flame speed measurements. The results showed that for the smallest size range $(0-10 \,\mu\text{m})$ and the largest size range $(53-75 \,\mu\text{m})$, flame speeds were ~ 4 cm/s while the two middle Al:Zr size ranges had flame speeds of only ~ 2 cm/s. The unexpected size dependence is attributed to a change in the thermal transport mechanism controlling flame propagation, from thermal conduction at small Al:Zr powder sizes to thermal convection at large sizes. The rate of energy release during the thermite reaction also plays a role in controlling the flame speed. We propose that the faster flame speed for the 0–10 µm Al:Zr particles result from more contact points between the fuel and oxidizer powders, leading to improved oxygen mass diffusion and greater energy release promoting thermal transport by conduction. In contrast, the faster speed for the largest 53-75 µm Al:Zr particles is attributed to increased thermal transport via convection due to larger pore sizes. The 10-32 and 32-53 µm Al:Zr particle sizes are either too big or too small for reactivity or thermal transport to be optimized, resulting in slightly slower flame speeds. These results show that larger Al:Zr particles can be designed to exhibit reactivity representative of smaller size particles by utilizing composite particles that leverage intermetallic reactions while also exploiting multiple modes of heat transfer.

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1. Introduction

Examining energy release from metal particle combustion is an active area of research that involves more than simply quantifying measurements, but also rationalizing fuel and oxidizer reaction and propagation mechanisms. The relative speed and intensity of these complex particle-to-particle interactions are usually measured using aggregated metrics such as flame speed that can be considered a macroscopic representation for particle reactivity. Metal particles inherently store high chemical potential energy (on both gravimetric and volumetric bases) and can be useful in applications such as enhanced blast explosives, thermites, bio-and chemical-agent defeat, and other high-energy pyrotechnic applications [1,2]. For example, metal fuels like aluminum (Al)

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store 31 kJ/g of chemical energy that can be released via oxidation reactions, while zirconium (Zr) stores 12 kJ/g. However, Zr is one of the hottest burning metal fuels with an adiabatic flame temperature of 4930 K, while Al is lower at 3732 K when reacting with oxygen. All of the values reported here are calculated using thermal equilibrium software that assumes complete oxidation in a pure oxygen environment and constant pressure conditions [3,4]. These idealized values provide an indication that heat of combustion is not the only criterion in determining combustion behavior of metals, and other factors such as the thermodynamic stability of the metallic oxide (combustion product), rate of reaction, and efficiency of conversion from reactants to products also contribute to an overall combustion performance analysis.

Combustion and Flame

Zirconium powder has a lower ignition temperature than aluminum, i.e., 1173 K [5] compared to 2213 K [6], respectively, and Zr powder is more sensitive to electrostatic discharge than Al powder (i.e., 5 - 40 mJ for Zr [7] compared to >100 mJ for Al [8] for similarly sized particles). For this reason, previous

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thermite studies using Zr included perchlorates, such as potassium perchlorate ($KClO_4$), that reduce the sensitivity of the composition to static electricity and increase safety in handling Zr powder [9]. In studies that examined the ignition temperature of Zr/KClO₄ and Al/KClO₄ using a hot bridge wire ignition source, results showed Zr/KClO₄ ignited at 573 K [10] while Al/KClO₄ ignited in excess of 773 K [11] and a higher ignition temperature is more desirable for a pyrotechnic igniter for safety reasons. However, Fathollahi et al. [11] showed significant incomplete combustion for Al/KClO₄ that limited its usefulness. Ji et al. [12] combined Zr and Al powder with KClO₄ in a weight ratio of 1:1:2 and studied its energy release behavior with the hope that they could desensitize the composition yet capitalize on Zr reactivity. They found no intermetallic reactions under thermal equilibrium analysis and Zr particles oxidized to near completion while only the surface of Al particles oxidized. They concluded that addition of Al raised the ignition temperature to > 773 K, but this formulation was plagued with incomplete combustion.

Aluminum is soft and ductile [13] while Zr is hard and brittle [14]. The contrast in mechanical properties was exploited using high energy ball milling to better mix Al with Zr thereby capitalizing on the intermetallic reaction between Al and Zr that can lower ignition thresholds. During the ball milling process Al deforms and cold-welds onto itself while Zr fractures [15] such that the final Al:Zr particles are a well-blended dispersion of Al and Zr. Forthcoming results from a concurrent study show that ignition thresholds of Al:Zr powders vary little with size when the powders are drawn from a single milling batch. The ball milled Al:Zr particles demonstrate intermetallic reactions that initiate between 300 and 600 °C and produce up to 30 kJ/mol [16].

Ball milled Al and Zr-based fuels show great combustion potential as they combine the favorable properties of high energy content from Al with the high flame temperatures of Zr. Previous studies on the combustion of Al:Zr particles have shown that they burn in a two-stage process, transitioning from an Al-vapor flame to a condensed state Zr burn after a critical amount of Al has evaporated from the molten composites [17,18]. The objective of this study is to examine the combustion behavior of Al:Zr particles as a function of particle size when combined with a solid oxidizer, molybdenum trioxide (MoO₃). Combustion of the thermite is analyzed by quantifying flame propagation speed in a burn tube. Further, a thermal energy transport model is developed to assess the influence of conduction and convection as a function of Al:Zr particle size in Al:Zr-MoO₃ flame propagation. To supplement modeling, additional experiments including differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are also performed to understand the heats of combustion and reaction kinetics unique to ball milled Al:Zr mixed with MoO₃ and as a function of Al:Zr particle size. Finally, powder X-ray diffraction (XRD) analysis of the product residue provides information on product species concentrations as a function of Al:Zr particle size.

2. Experimental

2.1. Materials

Aluminum-zirconium (Al:Zr, 1:1 atomic ratio) composite fuel particles were synthesized by ball milling stock powders of aluminum (Alfa Aesar, 99.5% pure, -325 mesh) and zirconium (Atlantic Equipment Engineers, 99% pure, -50 mesh) using a planetary Retsch PM400 ball mill. The composite fuels were milled for an hour at a ball-to-powder ratio (BPR) of three using hexane as a process control agent (PCA). The as-milled particles were sieved dry for at least three hours to the ranges of 0–10, 10–32, 32–53 and 53–75 μ m. The particle size distribution of each sieved range was measured by a Horiba LA-950V2 particle size analyzer with



Fig. 1. The four Al:Zr particle size distributions with each sample showing significant differences between their mean particle size.



Fig. 2. Thermal chemical equilibrium code simulations for adiabatic flame temperature (AFT) and heat of combustion (HOC) at different equivalence ratios for Al:Zr-MoO₃.

isopropanol as the scattering medium and the sieved ranges are shown in Fig. 1.

Each Al:Zr size range was mixed with molybdenum trioxide (MoO_3) powder to a stoichiometric ratio. This mixture ratio was chosen based on heat of combustion and adiabatic flame temperature simulations calculated using REAL code [3,4] to determine optimal mixing ratios. The highest adiabatic flame temperature and heat of combustion are 3840K and 3732 kJ/kg, respectively for a stoichiometric equivalence ratio, shown in Fig. 2. The MoO₃ powder (Sigma Aldrich) consists of particles with a plate-like morphology, thickness less than 100 nm and rectangular platelet structure of 1–3 µm length. Batches of approximately 900 mg were prepared with a mass fraction of 41.3% fuel (Al:Zr) and 58.7% oxidizer (MoO₃).

Table 1

Density measurements for Al:Zr samples with various particle size distributions that are indicated in the top row.

Al:Zr	0–10 µm	10–32 µm	32–53 µm	53–75 µm
Mean density (g/cm ³)	5.07	5.00	4.97	4.91
Standard deviation	0.07	0.02	0.05	0.02

To mix the thermites, both fuel and oxide particles were placed in 80 ml of hexane and sonicated in a Misonix 3000 (Qsonica) Sonicator for a total of 2 min at 10 s intervals; hexane was used as the mixing process control agent (PCA) and was also used as the ball milling PCA, as described previously. After sonication, samples were dried for 24 h in a fume hood then reclaimed using a grounded brush. These steps were taken for each of the four different Al:Zr size ranges.

The powder mixtures were loaded into 7 cm long quartz tubes with an inside diameter of 3 mm and outside diameter of 4 mm using a funnel facilitating a homogeneous distribution of particle packing that is consistent for each sample. This procedure helps eliminate density gradients within the samples that lead to discontinuities in flame propagation. The transparent tube apparatus has been used extensively to measure flame propagation behavior in thermites [19–25] and provides a one-dimensional (axial) perspective that can be visualized with high speed imaging diagnostics.

2.2. Theoretical maximum density

Density measurements were made for each Al:Zr size range using a Micromeritics AccuPyc II 1340 Gas Pycnometer and the mean density with standard deviation in measured values are shown in Table 1. The small variation in measurements imply uniform chemistry of the powder across all particle size ranges. Density measurements of Al:Zr were used to determine the mass ratios of fuel (Al:Zr) to oxidizer (MoO₃) powder for each mixture.

Eq. (1) is used to calculate a theoretical maximum density (TMD) for the mixture. The TMD is the highest material density that can be quantified for a given volume because the calculation assumes no void space. The apparent bulk density (ρ_{mix}) is the mass of the powder divided by the volume the powder occupies that includes the space between particles. The final bulk density of the mixture is expressed in terms of the percentage of TMD shown in Eq. (2).

$$TMD = \sum_{k=1}^{n} \left(M_k * \rho_k \right) \tag{1}$$

$$%TMD = \rho_{mix}/TMD * 100 \tag{2}$$

In Eq. (1), M_k and ρ_k are the mass and density of each material in the mixture summing over all reactant species (k), and ρ_{mix} is the mixture apparent bulk density determined by dividing the total mass of the mixture by the total volume occupied by the powder. The oxidizer density remains constant at 4.69 g/cm³ while the fuel density ranges with the values in Table 1. The experiments were designed to maintain a constant bulk density reported in terms of percent TMD and was 35%TMD.

2.3. High speed imaging and data processing

Ignition was achieved using resistive heating of a nichrome (NiCr) wire with supplied 24 V and 15 A from a 360 Watt DC Power Supply. The wire was positioned into the powder at one end of the tube. The reaction was recorded using a Phantom v2512 (Vision Research) high speed camera with a 50% neutral density (ND) lens filter applied to both reduce image saturation and achieve sufficient light intensity. The camera recorded with a resolution set



Fig. 3. Representative control area filled with ranging particle sizes of Al:Zr and MoO_3 . Red circles correspond with Al:Zr particles and blue circles correspond with MoO_3 assumed to fit within the void space. Two parallel thermal circuits are shown corresponding to Eq. (3) and Eq. (4), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to 1280×128 pixels and a frame rate of 30,000 frames per second. Once recorded, videos were analyzed using a custom MATLAB script. The images were processed by transferring pixel values into a large matrix (the size of the resolution). Pixels with maximum intensity from each column in the matrix were identified for each frame and tracked as a function of time to resolve flame speed. The maximum intensity and corresponding location were then plotted as a function of time to compute a velocity of the flame front with 99% accuracy.

2.4. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was performed on the Al:Zr samples with MoO_3 to assess the heat output and nearequilibrium kinetics of the oxide reactions. Each stoichiometric mixture was heated under Ar from 100–1100 °C at 40 °C/min in a TA Q600 DSC. The mixtures were heated twice, which allowed for baseline subtraction of effects of the furnace or reversible reactions such as Al melting. The resultant baseline-subtracted traces were analyzed for the total heat by integrating from 600–1100 °C.

2.5. Thermogravimetric analysis

A NETZSCH STA 449 thermal gravimetric analyzer was used to provide kinetic analysis of the Al:Zr and MoO₃ particles. The TGA was calibrated with calcium oxalate and the weight loss/onset of weight loss values were within 1.0% of reported literature values. Powder mixtures of 8 mg were loaded into alumina crucibles and experiments were performed in a controlled environment of 80:20 nitrogen to oxygen gas mixture at a flow rate of 100 ml/min.

2.6. Powder X-ray diffraction

Product residue from the Al:Zr-MoO₃ flame speed reactions was collected for analysis of crystalline species using powder X-ray diffraction (XRD). Experiments were performed using a Rigaku Ultima III powder diffractometer. Data were collected from 15–60° 2θ with parallel beam geometry in continuous θ – 2θ mode at 2°/min with a step size of 0.02°. The XRD results were analyzed using MDI Jade V9.1.1 software both for quantitative and qualitative analysis.

2.7. Thermal transport model

A thermal resistance model of an inter-particle control area was developed to assess the role of thermal transport in flame propagation as a function of Al:Zr particle size. The control area was filled with spherical particles stacked directly on top of each other (see Fig. 3). One-dimensional thermal resistance was calculated



Fig. 4. (A) Flame speed as a function of Al:Zr particle size for the Al:Zr-MoO₃ stoichiometric mixtures at a constant bulk density of 35% TMD. Numbers in bar represent average flame speed and standard deviation in the measurements are shown by the lines on the top of the bars. (B) Sequence of time stamped still frame images of flame propagation for 0–10 µm Al:Zr-MoO₃. All Al:Zr particle size mixtures exhibit phenomenologically similar propagation behavior.

using two parallel resistors as illustrated in Fig. 3 and described in Eqs. (3)-(5).

$$R''_{fuel} = n_f R''_{AlZr} + n_c R''_{cp}$$
(3)

$$R_{ox}^{\prime\prime} = n_{\nu} R_{MoO3}^{\prime\prime} \tag{4}$$

$$\frac{1}{R''} = \frac{1}{R''_{fuel}} + \frac{1}{R''_{ox}}$$
(5)

In Eq. (3), $R_{AlZr}^{"} = D_{AlZr} / K_{AlZr}$ and in Eq. (4), $R_{MOO3}^{"} = D_{MOO3} / K_{MoO3}$ where K_{AlZr} and K_{MOO3} are the thermal conductivity of Al:Zr (235 W/mK) and MoO₃ (138 W/mK), respectively [26]. Also, D_{AlZr} is the diameter of the Al:Zr particles, D_{MOO3} is the diameter of MoO₃ that is assumed to fit within the void space between Al:Zr particles. Also, n_c , n_f and n_v represent the number of contact points, fuel particles and voids for each particle size range that fit within the control area, respectively. The contact resistance at the Al:Zr particle interface $(R_{cp}^{"})$ is assumed to be 2.75 m²K/W, i.e., the contact resistance of an aluminum interface in an air environment [26]. Total thermal resistance is $R_{i}^{"}$ and calculated in Eq. (5) by summing the two resistive series in parallel (see Fig. 3).

3. Results and discussion

Initial flame speed testing was with pure Al:Zr to assess any indication of self-propagation due to the intermetallic reactions. Generally, self-propagating thermite reactions must have an adiabatic flame temperature that exceeds 2000K [1]. Thermal equilibrium calculations for the Al:Zr reaction show the flame temperature is 1803 K, suggesting that Al:Zr powder alone will not self-propagate. Experimentally, the Al:Zr particles directly in contact with the NiCr wire ignited, but self-propagation did not occur; indicating an additional solid oxidizer is required to generate enough energy to propagate the reaction forward beyond the ignition source. Thermal equilibrium calculations for Al:Zr-MoO₃ (where Al:Zr-MoO₃ notation denotes a stoichiometric mixture of Al:Zr and MoO₃) show the adiabatic flame temperature is 3841 K (see Fig. 2), and a self-propagating reaction was observed. It is noted that Al:Zr powders dispersed in air and O2 (without the presence of a secondary oxidizer powder) have been shown to burn between 2800-3500K [17].

Figure 4a shows the measured flame speed for each $Al:Zr-MoO_3$ mixture and Fig. 4b illustrates a sequence of representative still frame images of flame propagation. The uncertainty in the average values are shown in the bar graphs as standard deviations (Fig. 4a). Note that the uncertainties are smaller than the variation

between mixtures such that there is a statistically significant variation in flame speed as a function of Al:Zr particle size. The largest standard deviation is associated with the slowest flame speed, but there is no consistent trend between standard deviation and flame speed. The highest flame speeds are for the smallest and largest Al:Zr powder sizes, which is counterintuitive since flame speed typically increases with decreasing particle size. The highest flame speed for the largest particle size may be attributed to a shift in the active thermal transport mechanism.

Figure 5 shows a correlation between higher flame speeds (FS) and reduced thermal resistance (R") as a function of Al:Zr particle size in the Al:Zr-MoO₃ mixtures. The trend suggests a coupling between the size of the Al:Zr fuel particles and the flame speed that is enhanced at the smallest and largest particle sizes. Reasons for this behavior are elaborated below, but generally imply a trade-off as a function of fuel particle size between the rate of chemical energy liberated and the effectiveness of modes of thermal transport including conduction and convection.

To better understand thermal transport within the particle mixtures, the Andreev (A_n) number is included in the analysis. The A_n number compares the role of convection to conduction in porous media [27], where an increase in A_n (Eq. (6)) implies convection is the more dominant mechanism. Constants required for the A_n calculation include apparent bulk density, ρ mix, and heat capacity, c_p of the Al:Zr-MoO₃ mixture. Other variables in Eq. (6) include the flame speed, FS, and the thermal conductivity of product gas, K_g . In Eq. (7), d_h is the hydraulic diameter, where A_o is the specific surface area of the fuel particles and ε is the porosity determined using Eq. (8), A_V is the total void area and A_T is the total area of the control area. These variables are tabulated in Table 2 and results of this analysis are shown in Fig. 5.

$$A_n = \frac{\rho_{mix} FS d_h c_p}{K_g} \tag{6}$$

$$d_h = \frac{4s}{A_o(1-s)} \tag{7}$$

$$\varepsilon = A_V / A_T \tag{8}$$

As the particle size increases from $0-10 \,\mu\text{m}$ to $32-53 \,\mu\text{m}$, the *An* number increases from 1.2 to 2.2 (Table 2 and Fig. 5). However, for the largest Al:Zr particle size range there is a three times increase in *A_n* number compared to the smaller three size ranges. Bobolev et al. [27] explain that there exists a threshold value for *A_n* where further increases in porosity will transition thermal transport from conductively dominated to convectively dominated. Bobolev et al. [27] found the *A_n* threshold to be 6 for an explosive (i.e., RDX) composite and Hunt et al. [28] observed a threshold of

l:Zr-MoO ₃ (μm)			0-10	10-32	32-53	53-75
omix S 1 _h A _n	Aj Po Hy Ai	pparent bulk density (g/cr prosity ydraulic pore diameter (m ndreev number	$\begin{array}{ccc} n^3) & 4.848 \\ & 0.136 \\ n) & 3.03 \times 10^{-6} \\ & 1.20 \end{array}$	$\begin{array}{c} 4.818\\ 0.095\\ 8.57\times10^{-6}\\ 1.97\end{array}$	$\begin{array}{c} 4.807 \\ 0.097 \\ 1.78 \times 10^{-5} \\ 2.20 \end{array}$	$\begin{array}{c} 4.780\\ 0.055\\ 1.45\times10^{-5}\\ 7.04\end{array}$
(s)	8					250
d (cm	7	4			An	
beed	6	1			11	200 Therr
meS	5	1		1	FS	nalR
& Fla	4			1		150 esist
(An)	4	•		1		100 ance
nber	3			1		(Km ²
v Nur	2		State Stat	and the second s	R''	50 🕅
dree	1	X		e **		
An	0	A			*	0

Fig. 5. Modeled thermal resistance (R"), Andreev number (An), and measured Flame Speed (FS) as a function of Al:Zr particle size for the Al:Zr-MoO₃ mixtures. Thermal resistance is in units of Km²/W with triangle symbols and flame speed in m/s with circle symbols. It is noted that the natural log of thermal resistance is plotted for ease of comparison.

0.18 for an intermetallic composite of Al and Ni [28,29]. The A_n numbers shown in Fig. 5 illustrate there is more convective dominance in energy transport with the larger Al:Zr particles. More convective heat transport will contribute to higher measured flame speeds (Fig. 4). Based off the values in Table 2, the critical transition threshold value of A_n for the Al:Zr-MoO₃ mixture must be somewhere between 2 and 7.

Table 2

In Fig. 5, the smallest Al:Zr particle sizes show a lower A_n number, indicating that thermal conduction dominates energy propagation. However, this smallest size range also shows a higher thermal resistance, indicating that energy transfer by conduction is not optimized, even though the flame speed is high. For all size ranges, the Al:Zr-MoO₃ oxidation reaction is diffusion controlled such that the oxidation reaction occurs at the interface of the fuel and oxidizer particles and is therefore limited by the diffusion of mass and energy transport influenced by interfacial contact. For the smallest Al:Zr particle size, there are a higher number of contact points such that diffusion oxidation will be enhanced and therefore more chemical energy is liberated during reaction; this, in turns, facilitates energy transport. As the size range increases, fewer contact points limit the diffusion-based, interfacial reactions, but heat transfer between burning particles within the flame increases as convection becomes more dominant and counterbalances kinetic limitations. To examine diffusion kinetics more thoroughly, DSC was used to quantify Al:Zr-MoO₃ reactions as a function temperature among the four sizes of Al:Zr powders.

Figure 6 shows DSC exotherms of both the intermetallic formation reactions and subsequent oxidation reactions between Al:Zr and MoO₃. These results provide an understanding of the solid and liquid material reactivity without significant contribution of oxygen from the surrounding environment and provides insight into the non-equilibrium reactivity of the flame propagation experiments. The baseline subtracted traces are shown as dashed lines in Fig. 6. The first small exotherm marks the formation of the Al₃Zr intermetallic [30,31] which shows good uniformity of onset and peak



Fig. 6. Heat flow from DSC analysis (Exotherm up, y-offset artificially added for clarity) Al:Zr-MoO₃ exhibiting uniform onset of the first intermetallic peak around 370 °C as a function of Al:Zr particle size. The high temperature (i.e., >600 °C) exotherms represent oxidation reactions.

temperature (onset of \sim 325 °C and peak temperature which varies by less than a few degrees) across the different Al:Zr particle size mixtures. This uniformity implies that the internal microstructure of the Al:Zr particles is similar as a function of size, such that ignition properties should also be similar since ignition of the metal fuels is primarily driven by the intermetallic formation reaction [31]. It is noted that thermites composed of discretely separate particles of Al, Zr, and KClO₄ do not exhibit the intermetallic reactions seen in Fig. 6 [12]. This demonstrates that ball milling of Al and



Fig. 7. Kissinger plots of reaction kinetics of Al:Zr-MoO₃. Each temperature reported is the peak temperature of the corresponding DTG plot. The legend corresponds to the Al:Zr size ranges in μ m.

Zr powders to form composite Al:Zr powders may be an essential processing step for exploiting the chemical energy released by the intermetallic formation reaction.

In Fig. 6 there are significant differences in the onset temperature for the exothermic reaction that appear just below the melting temperature of Al (660 °C). At this point, condensed-phase oxygen transfer is thought to occur until MoO₃ begins to decompose at ~700 °C [32]. The trends of decreasing onset temperature and increasing heat output as Al:Zr particle size decreases are attributed to greater interfacial contact between the smaller fuel particle sizes and the oxidizer and thus earlier and greater heat release due to metal oxidation.

A TG analysis was performed up to 900 °C and the Al:Zr-MoO₃ samples were examined at varying heating rates. There is about 2.5% mass gain with temperature increase from 500–900 °C for all Al:Zr sizes and at each heating rate. By varying the heating rate (i.e., 10, 20, 30 and 40 °C /min), apparent activation energies for oxidation were determined using the peak temperature fits to the Kissinger kinetic model using Eq. (9) [33] as shown in Fig. 7. Heating rate is represented by β and T_{α} is absolute peak temperature, E_a is the apparent activation energy and *R* is the gas constant.

$$\ln \beta / T_{\alpha}^2 = \text{Constant} = E_{\alpha} / R T_{\alpha}$$
(9)

For thermites, it has previously been shown that lower apparent activation energies correlate with higher flame speeds for both conductively and convectively dominated reactions [34,35]. From Fig. 7, for the largest 53-75 µm and smallest 0-10 µm Al:Zr particle sizes, apparent activation energies are larger at 215 and 232 kJ/mol, respectively and flame speeds are higher. In contrast, the apparent activation energies for the $10-32\,\mu m$ and $32-53\,\mu m$ Al:Zr size ranges are smaller at 139 and 135 kJ/mol, respectively, and the flame speeds are lower. These correlations appear to contradict the relationship between apparent activation energy and flame speed that are reported in [34,35]. However, in those studies the dominant heat transfer mechanism (i.e., convection or conduction) remained constant for all mixtures evaluated. Specifically, in Kappagantula et al. [35] and Farley et al. [34], flame propagation never experienced a transition between convection and conduction-dominated mechanisms within the same formulation. In this study, the largest Al:Zr particle size Al:Zr-MoO₃ mixture is convectively dominant (see Fig. 5 A_n number) while the smaller three mixtures are conductively dominant. Due to less efficient conductive energy transport in the middle particle size ranges,

Table 3

Product species weight percent concentration identified from powder XRD Rietveld Refinement analysis of the residue from Al:Zr-MoO₃ flame speed reactions for all Al:Zr size ranges.

Product species	Al:Zr	Al:Zr	Al:Zr	Al:Zr
	0–10 μm	10–32 μm	32–53 μm	53–75 μm
MoO_3	30	29	59	58.3
ZrO_2	30	32	11	11.1
Al_2Zr_3	2	2.8	4	2.5

despite lower apparent activation energies, they may require more time to transfer energy, thus reducing flame speed.

The vertical axis intercept in Fig. 7 for each mixture is an indication of the pre-exponential factor for the Arrhenius reaction, which relates to the rate constant for oxidation [36]. For the smallest Al:Zr particle size mixture, the pre-exponential factor is higher than the other three Al:Zr mixtures (Fig. 7) and indicates that the oxidation kinetics are faster for the smallest Al:Zr mixture. This is an important result and consistent with the theory proposed here that predicts higher flame speeds for the smallest Al:Zr mixture due to faster interface oxidation reactions while the particles are in close contact.

Powder XRD was performed on the products of the Al:Zr-MoO₃ flame speed reactions and results are shown for the weight percent of selected compounds in Table 3. The powder XRD data is made available in Supplementary Information. For the smaller Al:Zr particle size mixtures, there is about half the amount of MoO₃ remaining after combustion compared to that of the larger Al:Zr particle size mixtures. The consumption of MoO₃ in the smaller Al:Zr particle size mixtures is an indication of more complete oxidation. A reverse trend is seen in the larger Al:Zr particle size mixtures where there is roughly half of the zirconia (ZrO₂) produced than that of the smaller Al:Zr particle size mixtures. That is, ZrO₂ (a primary product of the oxidation reaction with MoO₃) is seen in greater abundance when more MoO₃ is consumed. Other work [12] has shown for discrete mixtures of Al, Zr, KClO₄, that Zr oxidation is favored over Al oxidation [12] consistent with results in Table 3 for the formation of ZrO₂.

Table 3 shows no Al_2O_3 in the product residue from all samples analyzed, likely because Al_2O_3 condenses from the vapor state and can form small nano-scale crystals which are difficult to detect via XRD. Table 3 also shows a small and consistent concentration of Al_2Zr_3 that suggests intermetallic reactions occur for all particle sizes but particles oxidize to other species, regardless of the Al:Zr particle size.

Results in Table 3 imply that due to the two-stage nature of the Al:Zr reaction (i.e., with Al burning first in the vapor state and Zr burning second in the condensed state) that the smaller particles are burning to greater completion evidenced by the increase in ZrO_2 content. The high interfacial contact of the oxide with the smallest Al:Zr particles may promote diffusion oxidation. Table 3 further implies that larger particles may quench before Zr in the composite can oxidize and may result from energy transport that is mechanistically different due to increased convective heat transfer. However, in the former case, enhanced oxidation kinetics remain dominant throughout flame propagation, allowing for more complete combustion (as seen in Table 3), while in the latter case convective flow causes particles to spread out in the propagating flame and quench.

All of these results illustrate the complex combination of metallic species, oxidation rates, thermal transfer, and timing of energy release are of great importance to the flame speed. These results warrant further study using methods such as spatially resolved high-speed emission spectroscopy that can identify intermediate chemistry in the reaction zone. Currently, it is unclear how the rate of production of the various oxide species (due to the two-phase nature of the composite burn) couples with heat and mass transfer mechanisms, but it is clear that particle size can be decoupled from overall reactivity through utilization of ball milled composite fuels over pure elemental fuels.

4. Conclusion

Ball milled aluminum with zirconium (Al:Zr) particles were prepared with four different Al:Zr particle size ranges (0-10, 10-32, 32-53 and 53-75 µm) and combined with molybdenum trioxide (MoO₃) particles. Thermite flame speeds were analyzed and results show that for the smallest and largest Al:Zr size ranges flame speeds were $\sim 4 \text{ cm/s}$ while the flame speeds for the two middle Al:Zr size ranges were $\sim 2 \text{ cm/s}$. The rate of energy release from the reaction and thermal conduction or convection are thought to be the major factors controlling the flame speed. Differential scanning calorimetry and thermal gravimetric analysis confirm that the smallest Al:Zr liberate more chemical energy and powder X-ray diffraction (XRD) analysis of product residue indicate more complete combustion. A heat transfer model was developed for the particle-to-particle heat transfer modes. Analysis of the Andreev number from this model indicates that the largest Al:Zr particle size mixtures experience a shift from conductive to convective energy transport. More efficient convective propagation increases the flame speed of the largest Al:Zr particle size thermite however the powder XRD results of the product residue indicate more incomplete combustion. These results show that the complex combination of intermetallic reactions, oxidation rates, modes of thermal transfer, and timing of energy release are of great importance to energy propagation and flame speed measurements.

Declaration of Competing Interest

All authors declare none.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.09. 028.

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