

Utilization of Industrial Waste Alloy as An Alternative to Micron-Al in Energetic Applications

by
Chenshuo Wang

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Aluminum-enhanced solid propellant is one of the most commonly used propellants. It is cost-effective, simple to store and handle, and energetic for thrust production due to the extremely high burning temperature of aluminum (Al) particles. However, a large-scale manufacturing of micro-sized aluminum powders with a narrow size distribution and high purification is still challenging, while the spontaneously formed oxidation layer on the surface of Al particles significantly reduce their reactive content. Here, we report on the feasibility of using AlSi10Mg micron particle, an industrial waste alloy from additive manufacturing with a median diameter of 13 μm , as a promising alternative for aluminum microparticles in propulsion applications. Compared to Al micron particles with a similar diameter, AlSi10Mg showed the comparable reaction temperature and activation energy. However, AlSi10Mg produced a much higher energy release, indicating its more complete oxidization as an alloy than Al particles with the inert Al_2O_3 shell. DSC-TGA results of the mixtures of those two micro-sized powders with CuO nanoparticles exhibited a similar reaction kinetics which indicates the involvement of gaseous oxygen. In combustion tests, the AlSi10Mg/CuO mixture showed a much shorter ignition delay compared to pure Al/CuO mixture, revealing its enhanced reactivity. The combustion rate of AlSi10Mg/CuO was found to be much higher than Al/CuO, and the thrust generation of AlSi10Mg/CuO was also more than 30% higher than Al/CuO in an atmospheric environment. Combustion of AlSi10Mg/CuO and Al/CuO in a low-pressure environment was also investigated. All these results indicated that micro-sized alloy particles recycled from the advanced manufacturing can replace Al micron particles for propulsion and energy production.

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1 Introduction

1.1 Motivation and Problem Statement

The high specific energy of micron-scale metal fuels makes them the promising candidates of energetic materials in various applications such as propellants, pyrotechnics, metal refining, welding, and explosives [1]. Commonly used metal fuels include micro-sized boron (B), magnesium (Mg), and aluminum (Al) particles [2]. Among them, boron has the highest theoretical oxidation specific heat at 58.86 kJ/g, being 1.9 times that of aluminum (31.01 kJ/g) and 2.3 times that of magnesium (24.75 kJ/g) [3]. Its abundance in Earth resources makes Al so far the most popular metal fuel [4] [5]. Nevertheless, the reactive content of micro-sized aluminum particles is low, due to spontaneous formation of its Al_2O_3 surface layer. And its combustion reaction mechanism suffers from the complex phase transformation processes associated with formation of Al_xO_y intermediates during the thermite reaction. The manufacturing cost is also high for production of high-purity aluminum particles.

Alloy generally is more chemically stable in ambient conditions (the room temperature and atmospheric pressure). Its manufacturing cost can therefore be significantly reduced, compared to pure metal. Some researchers have studied aluminum alloys as metallic fuels, such as Al-Si and Al-Mg [6] [7]. Since these alloys are more resistant to oxidation than metals, longer-term fuel storage is facilitated by preventing aging. The energetic performance of these aluminum alloys, on the other side, was found to be comparable to the pure aluminum particles. There is still a lack of detailed studies on the reaction

mechanism involving alloys, especially the role of the Al-metal bonds in a triple metal alloy which has been widely used in additive manufacturing. Further studies are needed to investigate both the thermochemical properties and combustion performance, in order to develop the aluminum-based alloys to replace pure metals as fuel.

1.2 The Research Objectives

The overall goal of this thesis is to investigate the energetic performance of the micron sized AlSi10Mg powder and its combustion mechanism, through comparing the structural and material properties to pure Al microparticles. Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and particle size analysis have been used to check the physical and chemical properties of the micron size AlSi10Mg powder. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been employed to understand the reaction mechanism and activation energy. A series of laser combustion tests have been performed to demonstrate the different combustion performances of micron-sized Al and AlSi10Mg based energetic mixtures.

1.3 Thesis Organization

Chapter 2 includes a literature review of the background of energetic material, covering the topics of thermite applications, the source of AlSi10Mg alloy, various methods to synthesis thermite, how the particle size affects the combustion performance, and available reaction mechanisms of metal fuels. Chapter 3 explains about the experimental details, including the method for synthesizing AlSi10Mg/CuO thermit and the instrument

setup. Major experimental results, such as combustion tests and the differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) results are presented and discussed in Chapter 4. Chapter 5 summarizes the thesis results and proposes the future work.

2 Literature Review

2.1 Metal Fuel and Energetic Materials

Formulations based on a combination of compounds that can release energy through an exothermic oxydo-reduction reaction are known as energetic materials. Several effects are produced with this energy. It may manifest as sound, heat, light, smoke, delay, thrust, or shock [8]. Some energetic materials are applied to the storage and release energy. Historically, commonly used energetic materials included RDX, TNT, and HMX[9], [10]. The heat released from these energetic materials is limited by the formed enthalpy, CO₂ and H₂O upon complete oxidation. Therefore, these materials have relatively low energy density compared to metal-based fuels. The maximal combustion enthalpy for metal fuels and monomolecular energetic materials is shown in Figure 2.1. Obviously, metal-based fuel exhibits higher energy densities than monomolecular energetic materials[11].

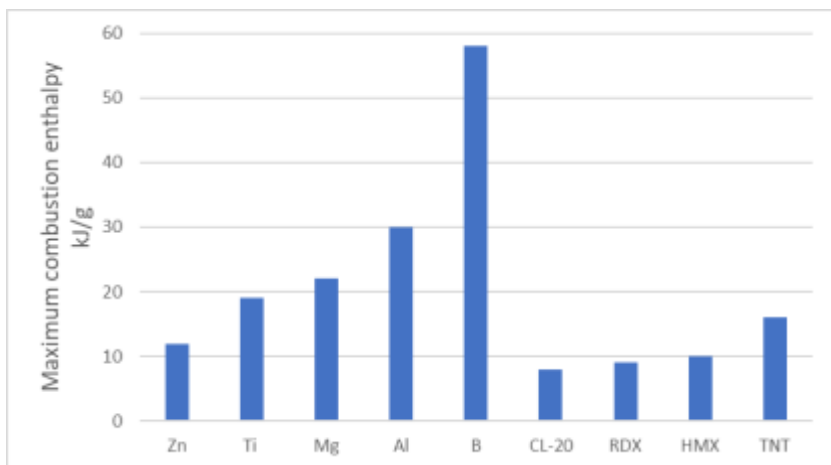


Figure 2.1 The maximum combustion efficiency for monomolecular energetic compounds and selected metal fuels [11]

In 1908, Goldschmidt defined Thermite as the exothermic reaction of aluminum with metallic oxides [12]. Thermite combines metal (Such as Al, Mg, B) and metal oxides (Such as CuO, NiO, Fe₂O₃) [13], which releases an amount of energy during the oxidation reaction [14]. The following equation (Equation 1



) represents an oxidation-reduction reaction. The metal oxide is denoted by the letter "AO" and the metal fuel by the letter "M" in the equation below. "MO" and "A" stand for metal oxide and metal, respectively, on the left side of the equation. " ΔH " stands for the reaction's entropy, which is the heat produced during the process [12].



The energy level in an exothermal reaction is depicted in Figure 2.2. The potential energy of the products is lower than the reactants in the exothermal, leading to heat generation or negative entropy.

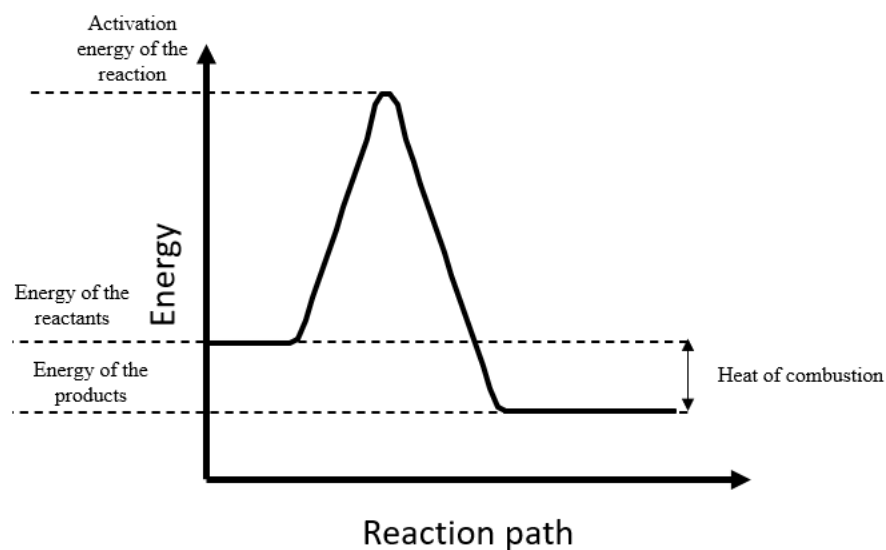


Figure 2.2 The energy level diagram of an exothermic reaction [15].

Involving enthalpy, Gibbs free energy must be understood. The following equation (Equation 2) exhibits the Gibbs free energy equation, " ΔG_r^O " is the Gibbs free energy, " ΔH_r^O " represents the enthalpy and " ΔS_r^O " refers to the entropy.

$$\Delta G_r^O = \Delta H_r^O - T\Delta S_r^O \quad \text{Equation 2}$$

The Gibbs energy indicates the spontaneity of the reaction. The Gibbs energy is negative magnitude, which is the spontaneous reaction. However, the reaction is not spontaneous when Gibbs energy is positive. The Gibbs energy is zero, which means the chemical reaction is chemical equilibrium. The thermite reaction is exothermal, where the product is solid, and the entropy does not change too much. Thus, the Gibbs free energy is negative in the thermite reaction, and it is a spontaneous reaction. The Ellingham diagram is an effective tool for analyzing the relationship between temperature and Gibbs free

energy, helping to select the suitable oxide to change the reaction process. According to Equation 2, the slope represents the entropy change and the stability of the formed metal oxide. The intercept of the y-axis refers to the change of enthalpy [16].

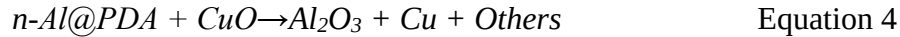
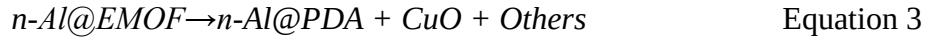
2.2 Classification of Highly Reactive Thermite

Al/metal oxide, Al/metal, Al/organic or macromolecule compound, and Al/inorganic compound are the four varieties of thermite energetic materials (tEM) [17]. Al/Fe₂O₃ is one of the classic Al/metal oxide thermite systems, which can be ignited by minimal energy and release exceptional energy, which is more than 3.9 kJ/g, with the maximum adiabatic temperature reaching around 3135 K [18]. The Y. J. Luo group applied a sol-gel process method to synthesis Al/ Fe₂O₃ thermite, increasing the reaction area for metal fuel and oxidizing agent, leading to heat release achieving 2.0kJ/g [19]. Al/CuO is another well-known tEM that has enough experimental evidence to support its high theoretical heat of reaction (~4.08 kJ/g) and high reactivity [20]. CuO can be shaped into porous, spherical, wire, rod, or tube shapes. Al/CuO therefore provides several unique structures to enhance combustion and ignite performance [17]. Yang et al. [21] reveals that core shell Al/CuO as energetic material system have lower ignition energy (10 mJ) and activation energy (181.142 kJ/mol).

Al/Metal tEMs are distinct and peculiar as metal-metal reacts. Both high reaction temperatures and efficient energy release are possible from the reaction [17]. Hence, the researchers are still exploring the potential value of Al/metal tEMs. The common

Al/metal tEM is Al/Ti and Al/Ni that can produced by an electrophoretic deposition method, output an excellent heat value of 316.2 J/g [22].

The mixture of Al/organic or macromolecule compound tEMs is gaining increasing attention. Polytetrafluoroethylene (PTFE), perfluoropolyether (PFPE), trinitrotoluene (TNT), hexanitrohexaazaisowurtzitane (CL-20), metal-organic frame (MOF), and other high-energy nitramines, are used as the organic compound in tEM because of their high substantial oxidation property [17]. Researchers developed a new type of energy-storage system using EMOF as the oxidizer and the exothermal reaction was studied into two processes (Equation 3 and Equation 4). The amount of heat release 4142 J/g and the lower ignition temperature at 301.5 °C was reported [23].



The ease of synthesis and low cost of inorganic materials make them appealing as oxidizers for tEM [17]. KMnO_4 , Na/KIO_4 , NaClO_4 are the common inorganic materials which have been used in thermite reaction. Al/ KMnO_4 is an energetic material system produced by Zachariah et al. [24] that has the advantage of quick reactivity over Al/ Fe_2O_3 , Al/ CuO , and Al/ MoO_3 .

2.3 Types of Al/Metal Oxide Thermite

Al/metal oxide is the prevalent combination in the thermite reaction system. Metastable metals can be used as fuel to participate in reaction. Boron (B), magnesium (Mg), and aluminum (Al) microparticles are mainly used as metal fuel. Boron has a high theoretical specific calorific value [25], Mg is very reactive [26] and Al is safe and stable compared to the other metastable materials [27]. Metal oxides which are widely used in the thermite reaction as oxidizer are iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3), molybdenum oxide (MoO_3), bismuth oxide (Bi_2O_3), and copper oxide (CuO) [28]. The heat of reaction, adiabatic reaction temperature, state of products, and gas production for various common thermites, including Al/CuO, Al/ Fe_2O_3 , Mg/CuO, and Al/NiO.

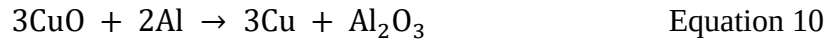
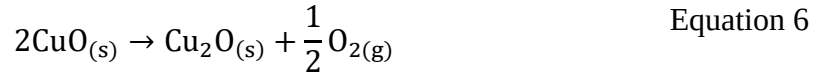
Table 1 The reaction properties for various common thermites [29]

Reactants	Heat of reaction (cal/g)	Adiabatic reaction temperature (K)	State of products		Gas production (gas / reactant)
			Oxide	Metal	
2Al+3CuO	974.1	5718	liquid	l-g	0.3431
2Al+ Fe_2O_3	945.4	4382	liquid	l-g	0.0784
Mg+CuO	1102	6502	solid	l-g	0.5201
2Al+3NiO	822.3	3968	liquid	l-g	0.0063

The Mg/CuO combination can release a large amount of heat and generate too much gas during the reaction process. Thus, Mg/CuO is not applicable for underwater welding or metal joining applications. On the other hand, Al/NiO produces less amount of gas, but it releases less amount of heat. The combustion performance for Al/CuO is moderate compared to the other combination. So, Al/CuO is widely used in the industry and aerospace, and there is sufficient data about reaction mechanism about the reaction for Al/CuO; that is why CuO is selected as the oxidizer in this thesis [29].

2.4 Micron-Sized Al/CuO Reaction Mechanism

In the initial state of the combustion process, Al is the metal fuel, and CuO is the oxidizer that is surrounded by air oxygen and nitrogen and the thermite activity of Al/CuO reaction needs 600 kJ kg^{-1} energy [30]. The entire thermite reaction mechanism for micron-sized Al/CuO is shown below [31]. First, the micron-sized Al melts at approximately 660°C , forming liquid phase Al (Equation 5). Two main reaction mechanisms are concluded, core Al diffuses through the alumina oxide shell or the aluminum oxide layer explodes as the temperature rises [32]. Then, CuO starts to decompose oxygen around $850\text{-}1000^\circ\text{C}$, and solid phase Cu_2O is produced with the decomposition (Equation 6) [33]. Liquid Al reacts with oxygen which is the thermite exothermal reaction and solid Al_2O_3 is formed during the thermite reaction (Equation 7). The solid copper melts at $1,085^\circ\text{C}$ (Equation 8) and the solid Cu_2O melts into liquid Cu_2O at around 1232°C (Equation 9) [34] [35].



2.5 Thermodynamics of Thermite Reaction

Zachariah's group employed the Dynamic Transmission Electron Microscope (DTEM) to investigate the reaction process between nanoparticles of Al/CuO, where the Al and CuO are 80 nm and <50 nm, respectively. In the initial state before heating, the Al nanoparticle appears in a sphere shape, while the CuO nanoparticle has an irregular shape. Upon heating, the prior nano shape transforms into a structure consisting of three large-scale, separate areas. Among these, the copper-rich central area displays the darker, while the surrounding regions, relatively brighter, are aluminum-rich and the morphology shape begins to change at 45 ns after heating. In the following, the copper oxide begins to melt and gradually forms a spherical shape at 235 ns; also, the aluminum nanoparticles aggregated around the copper oxide area at 425 ns [36].

The laser pulse heating method delays the onset of particle coalescence, in contrast to the conventional heating method. The melting point of Al and CuO nanoparticles are 933K and 1600 K respectively [36]. Because Al nanoparticles have a lower melting point in the

usual approach, they invariably melt before CuO. Nevertheless, with laser heating, the CuO nanoparticle melts before the Al does. This may be confirmed using calculations utilizing the Mie solution to Maxwell's equations, which show that the CuO nanoparticles absorb roughly three times more energy from 532 nm light than the Al particle [37]. Therefore, CuO nanoparticles melt before aluminum.

2.6 Thermite Application

Thermite has widespread application in gas generators, micro propulsion systems, welding, electric igniters, and ammunition primers, based on its advantages in high adiabatic flame temperatures, fast flame propagation velocity, and high energy density [38] [40]. Because it is inexpensive and does not require electricity, thermite is widely used in welding. The main fuel in this thermite reaction is metallic aluminum, which combines with Fe_2O_3 to produce molten iron alloy and Al_2O_3 . The resulting molten Fe alloy was then inserted for fusing between the two components. Every 439 meters of railroad track has one thermal reaction welding joint [40].

Thermite welding is appropriate for use in vacuum or underwater conditions, as well as railway welding where oxygen is scarce. Thermite rail welding did have several disadvantages, though. For example, during the welding process, particles or pores may mix with the welding area. Furthermore, non-fully fused rail sections may be vulnerable to metal fatigue [40].

Solid propellant is another use for thermite; it was created and employed by the Chinese more than 2,000 years ago [41]. Micron-sized propellant is now commonly used in the aerospace industry for tasks like orbit reduction, orbit transfer, and orbit maintenance for microsattellites [41]. Initially, the propellant is mixed with Al flakes or powder to raise the flame temperature and specific impulse [42]. Second, aluminum has the advantage of having high output energy qualities, being abundant on Earth, and being relatively safe, which makes aluminum the primary fuel for propellants. [42]. Modern thermite contains polymeric binders in addition to Al to improve propulsion performance [41].

2.7 Sample Size Affects the Combustion Performance.

The main element influencing the explosive performance is the size of the particle sample [43]. There was a discernible variation in the rate of combustion of aluminum particles at the nano and micron sizes. Nanoscale particles exhibited lower ignition temperatures and higher combustion rate compared to their micron-sized particles [44], due to the enhancement of catalytic activity by augmenting, which increases the surface-to-volume ratio [45]. Stated differently, a greater reaction area was made possible by smaller particle sizes, which allowed for a higher rate of reaction between the oxidizer and more reactants [43]. The diameter of micron-sized particles, which relates to the nth power of the particle diameter, limited their ability to burn [43] [46]. Thermogravimetric Analysis (TGA) curve for micron-sized Al particles displays a trend to 1450 °C in temperature. The steepest slope is seen in the plot for the size range of 1-2 μm and 3-4 μm ; the slopes for particles 45 μm and 75 μm are comparatively moderate. It goes without saying that smaller particles react more quickly [43].

The DSC-TGA results for micron- and nano-sized aluminum (Al) display that the micron-sized Al melting point in the figure is 659.7°C, whereas the nano-sized Al melting point is marginally lower at 656.3°C [47]. The reason for the variation in melting point is that surface energy is increased by nanoparticles. Furthermore, the heat required to melt micron-Al is 345.0 J/g, which exceeded nano-Al 199.4 J/g. The thermal characteristics of nano- and micro-sized particles are illustrated by these variations. The onset temperature of the TGA curve shows that nano-Al is more reactive than micron-Al; the former has an onset temperature of 470°C, while the latter has a lower onset temperature of 385°C [47].

2.8 Additional Metal Components Increase Reactivity.

Sample size is decreased by increasing aluminum thermite's reactivity. An alternative strategy to achieve this goal is to boost the mixture's heat reactivity by adding metals like magnesium (Mg). An additional 10% micron-sized Mg in nano Al/CuO thermite can raise heat flow from 949.5 to 2168.6 J g⁻¹, which is twice than the nano Al/CuO thermite [47].

2.9 Comparison of the Combustion Performance For Various Synthesis Methods.

The synthesis procedure has an impact on the combustion performance. The Al/CuO thermite can be synthesized using three main techniques: mechanically mixing (MM), precipitation (PC), and displacement (DP). The conventional method for synthesizing thermite is mechanical mixing. In the precipitation method, Al powder mixed with and

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and an ammonium hydroxide solution for 3h, and dried in the desiccator for 12h. In the displacement (DP) method, reduces Cu^{2+} to the Cu in the present of Al nano powder in galvanically reaction for generating the Al/Cu core-shell particles. Then, annealing the Cu results on the surface of Al to micro-Al/CuO core/shell particles. The PC and DP methods offers a shorter ignition delay and higher combustion efficiency [48].

2.10 The Application of AlSi10Mg

The Al-Si-Mg alloy's has lower density, strong mechanical qualities, outstanding casting properties, and heat treatment capabilities which make it a popular choice for a variety of applications, including the aerospace and automotive industries [49]. While adding silicon content improves the alloy's ductility and strength, it also makes production more challenging [50]. AlSi10Mg is a hypoeutectic alloy in the Al-Si-Mg alloy family that is well suited for additive manufacturing because of its narrow solidification range, which lowers the likelihood of hot cracking during the cooling process [51]. AlSi10Mg is a hypoeutectic alloy in the Al-Si-Mg alloy family that is well suited for additive manufacturing because of its narrow solidification range, which lowers the likelihood of hot cracking during the cooling process. The selective laser melting (SLM) is a mainstream approach for manufacturing AlSi10Mg alloy component, which offers the advantage of being high reliability, and cost-effectiveness [51]. AlSi10Mg alloy parts manufactured using SLM technology have higher tensile strength and hardness than conventional methods [52]. The primary chemical composition of AlSi10Mg is Al and

9.99% of Si, 0.44% of Mg. The remaining component of nearly 1% is Fe Ti Ni Mn Cu P [53].

2.11 Experimental Instrument

In the thermite reaction there are several instruments and techniques that are necessary for studying thermite reaction which are listed in the following.

2.11.1 High Speed Camera

The high-speed camera is employed to record the entire combustion process with Photron FASTCAM Viewer software (version 3.6.9.1). The combustion ignition delay and combustion duration are determined from the recorded video. These record data can help researchers to compare the performance difference in the combustion applications.



Figure 2.3 Photron FASTCAM fast camera

2.11.2 Differential Scanning Calorimetry and Thermogravimetric Analysis

Differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) are employed to analyze and determine what happens to materials during the heating process [54]. The TGA result displays the mass change over time with temperature changes. Along with the change in mass, many physical phenomena also appear, which included phase transitions, thermal decomposition and oxidation. In this thesis, TGA is a valuable instrument to determine the onset of oxygen release from the oxidizer and the initiation of the exothermic reaction between the metal fuel and oxygen. The DSC results reveal how much energy is released from the exothermal reaction, melting points and onset temperatures for each sample. With the temperature increase, exothermic and endothermic peaks appear, which indicate energy absorption with phase transitions and energy release from chemical reactions.



Figure 2.4 The NETZSCH STA 449 F3 Jupiter DSC machine used for this thesis

2.11.3 X-ray Diffraction

X-ray diffraction (XRD) is an effective technique to determine the crystallographic structure of a sample [55]. The working principle of the XRD is to measure the intensity and scattering angle of incident X-rays when X-rays pass through a material [56]. The following equation is Bragg's Law

$$n\lambda = 2d \sin \theta \quad \text{Equation 11}$$

In this equation, λ represents the X-ray wavelength, d is the spacing of the crystal layers (path difference), θ is the incident angle (the angle between the incident ray and the scattering plane), and n is an integer. The XRD tests are performed using a Panalytical X'pert pro in this thesis. The scanning range was $10 - 80^\circ$ with a step of 0.02° .

2.11.4 Scanning Electron Microscopy /Energy Dispersive X-ray Spectrometer

Scanning electron microscopy (SEM) is commonly utilized to get high-resolution sample images and detailed sample information [57]. The fundamental principle of SEM involves directing a focused beam of electrons to scan the sample's surface. Some SEM instruments have the resolution 1 nanometer. In this thesis, researchers used a Hitachi SU5000 SEM to verify the shape and size of the sample particles.

However, only SEM is not enough to explore microstructural details, and energy-dispersive spectroscopy (EDS) is also utilized in this thesis. The Energy Dispersive

Spectrometer (EDS) is an advanced instrument to analyze the chemical characterization/elemental of materials [58]. The EDS technique can additionally determine the elemental composition or distribution [59]. Oxford EDS system is utilized in this thesis.

2.11.5 Particle Size Analysis

The particle size analyzer plays an important role in evaluating particle size, which is a key parameter in combustion research. Particle Size analysis provides a precise method to determine the particle size distribution in a test sample. The working principle of particle size analyzer is based on the relationship between light scattering and particle size. Larger particles have smaller scattering angles, resulting in higher scattering intensities. A laser-based particle size analyzer is selected for this thesis because the sample particles cannot remain suspended and evenly distributed in the solution. The instrument used in this thesis is Mastersizer 3000.

3 Experiment

3.1 Synthesis Methods

AlSi₁₀Mg particles (<20 µm) are obtained from AP&C (Saint-Eustache, QC, Canada) as a waste-stream by-product from the SLS 3D printing process and are used as received. Micro-size Al (10 µm) and CuO (500 nm) particles are purchased from US Research Nanomaterials, Inc (Houston, TX). The water content is less than 0.1% in the experimental ACS-grade ethanol.

To synthesize the thermite composite, the AlSi₁₀Mg and CuO powders are added into 10 ml absolute ethanol and 50 mL beaker. Then, the solution is vigorously stirred for 10 minutes on a magnetic stirrer at 250 rpm to obtain homogeneous dispersion. Subsequently, vacuum filtration is used to filter thermite powder from the dispersion. Finally, the wet thermite is transferred to the oven to dry at 80 °C for 12 hours.

Equivalence Ratio (ER) is defined as the ratio between the actual fuel/oxidizer and the stoichiometric fuel/oxidizer [60]. In this research work, the effect of different ER values (0.6, 0.8, 1.1, 1.4, and 1.8) are evaluated and calculate according to ER (Φ), Equation 12.

$$\Phi = \frac{(n_{\text{AlSi}_{10}\text{Mg}}/n_{\text{CuO}})_{\text{actual}}}{(n_{\text{AlSi}_{10}\text{Mg}}/n_{\text{CuO}})_{\text{stoichiometry}}} = \frac{(n_{\text{Al}}/n_{\text{CuO}})_{\text{actual}}}{(n_{\text{Al}}/n_{\text{CuO}})_{\text{stoichiometry}}} \quad \text{Equation 12}$$

According to this equation, individual masses of Al, AlSi₁₀Mg and CuO are determined to produce 500 mg final mixture of metal/oxidizer powder as shown in Table 2

Table 2 Chemical compositions of energetic powders with different values of the equivalence ratio

Φ	Final Powder	AlSi ₁₀ Mg+CuO		Al+CuO	
		AlSi ₁₀ Mg	CuO	Al	CuO
0.6	500mg	66.7mg	433.3mg	59.5mg	440.5mg
0.8	500mg	85.1mg	414.9mg	76.3 mg	423.7mg
1.1	500mg	110.0mg	390.0mg	99.2mg	400.8mg
1.4	500mg	132.1mg	367.9mg	119.8 mg	380.2mg
1.8	500mg	157.9mg	342.1mg	144.1mg	355.9mg

3.2 Combustion Instrument Setup

A typical test, a 75mg thermite sample is loaded into a 5cm long transparent acrylic tube with an inner diameter of 1/8 inch and an outer diameter of 3/8 inch. The transparent acrylic tube is attached to a metal screw base by epoxy, which is then screwed onto a Dytran 1051v2 force detector in the center of the combustion chamber. A Phantom v2012 high-speed camera records the combustion process at 200,000 fps with 285 ns exposure time. The thermite sample is ignited by a 5W continuous wave 532nm laser for a duration of 400ms at 75% intensity. A Tektronics AFG1022 function generator is applied to trigger the oscilloscope and the high-speed camera simultaneously.

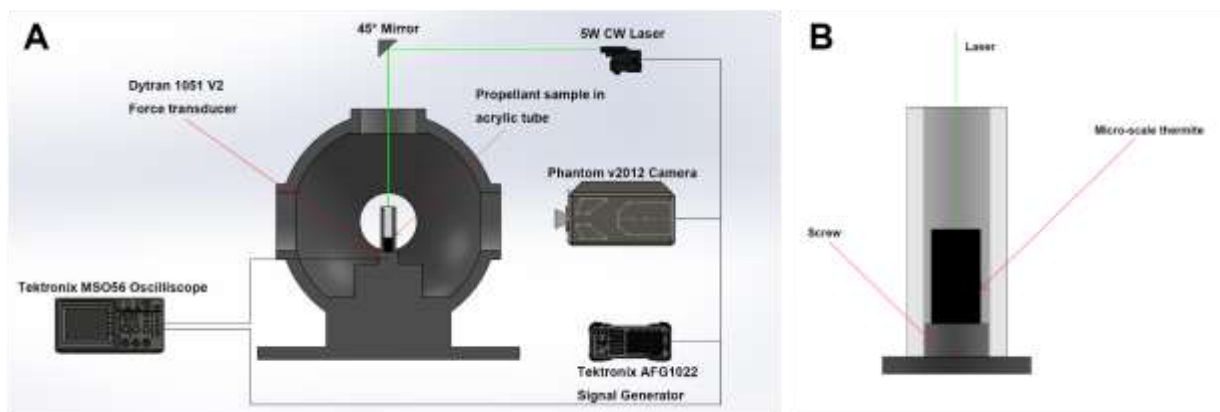


Figure 3.1 Combustion system (A) Laser ignition and high-speed camera set up (B) Combustion sample tube configuration

3.3 Differential Scanning Calorimetry and Thermogravimetric Analysis

Differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) analysis are carried out using a NETZSCH STA 449 F3 thermal analyzer. The measurements of pure fuel powder (AlSi10Mg and Al) are carried out in a mixed N_2 - O_2 environment with the oxygen flow rate at 10 ml/min and the nitrogen flow rate at 190 ml/min with a heating rate at 20°C/min from room temperature to 1500°C. The measurements of the thermite mixture are conducted under the protection of argon gas at 200 ml/min to avoid the presence of gaseous oxygen, with the heating rate 20°C/min from room temperature to 1500°C.

4 Results and Discussion

4.1 Material Characterization

Size and morphology are key factors to the reactivity of particles in energetic reactions. Therefore, multiple measurements are carried out for these understandings. SEM-EDS is applied to assess the microstructure of AlSi10Mg as well as to analyze its chemical composition, as shown in Figure 4.1. All particles are found to be smaller than 20 μm , corresponding well with the indication from the manufacturer, making the alloy particles unsuitable for SLS additive manufacturing. The particles also exhibit nearly perfectly spherical shapes. However, the particle size is not consistent. As shown in Figure 4.1 A, the particle diameter measures approximately 10 μm , and in the vicinity of the larger particles, smaller particles with diameters of roughly 5 μm are observed. The subsequent Particle Size Analysis can provide more precise details regarding particle size.

The EDS images, conversely, indicate that different elements are identically distributed in the particles, confirming the existence of alloy within the particles. The tabulated data below presents the elemental composition ratio within the AlSi10Mg particle. The ratio of Al, Si, and Mg is found to be roughly 85:10.5:1, with oxygen content less than 5%. The ratio matches quite well with the formula AlSi10Mg with Si taking roughly 10% of the total mass and Mg having around 1%. Please note that there can be some errors for the content of oxygen from EDS due to its error for smaller elements, as well as the presence of oxygen in the background carbon tape.

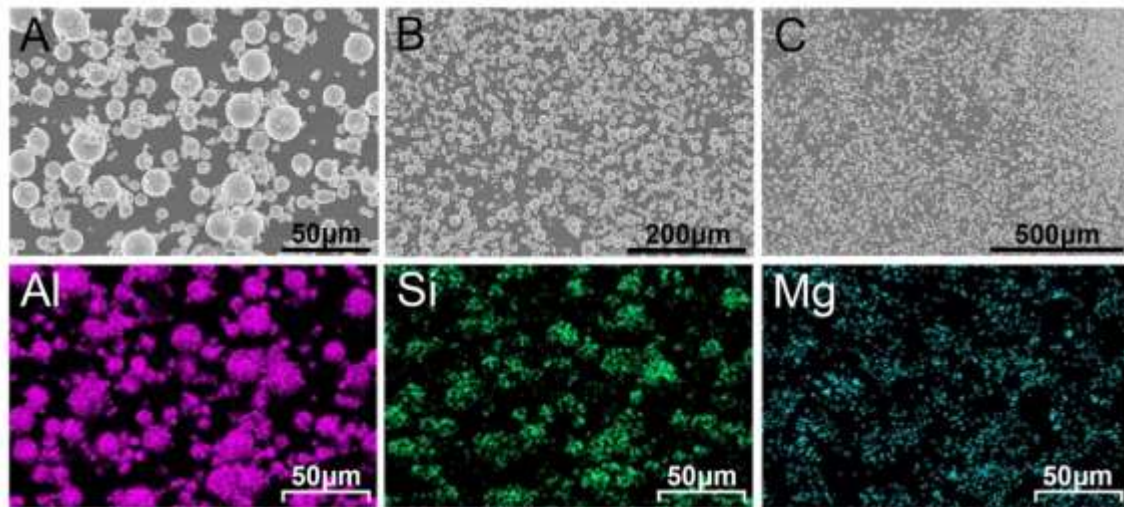


Figure 4.1 SEM image and EDS mapping of micro-size AlSi10Mg

Table 3 The weight ratio of AlSi10Mg from EDS analysis results

	Al	Si	Mg
Weight ratio	82%	10.5%	1%

XRD measurement is utilized to confirm the crystal structure of the as-received AlSi10Mg powder, offering more reliable means of verifying the composition of the alloy. Figure 4.2 presents the crystal phase composition of the alloy powder of AlSi10Mg. The most prominent peak of AlSi10Mg corresponds to the Al reference due to the high aluminum content in the alloy. Minor peaks corresponding to Si are also found. Some less conspicuous peaks indicated the presence of magnesium (Mg) due to its less content.

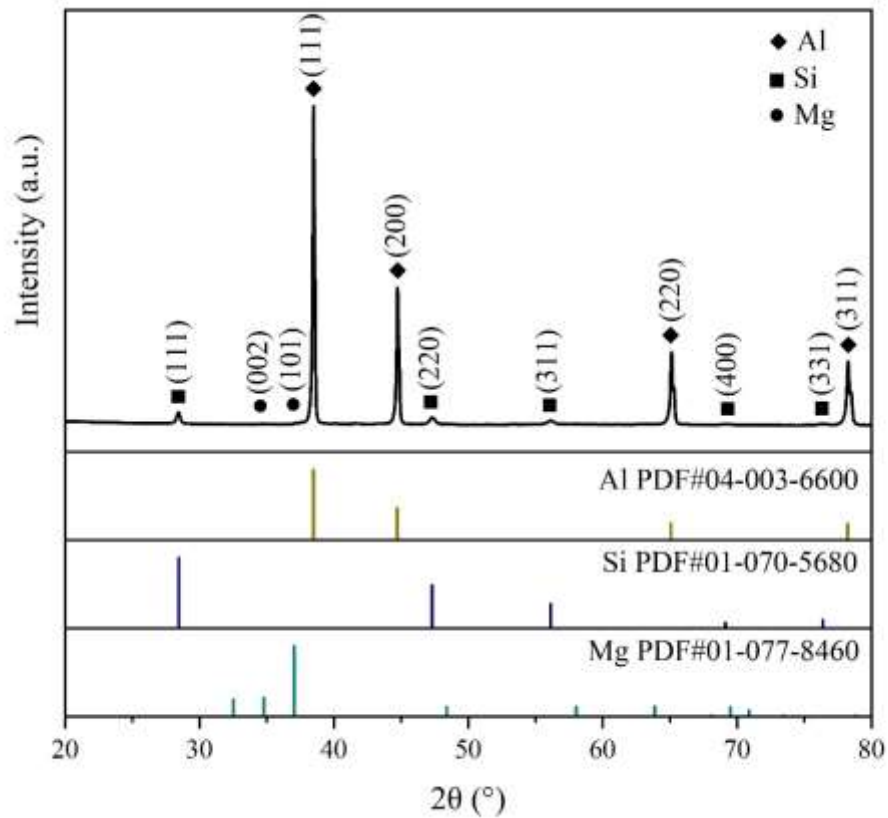


Figure 4.2 The XRD comparison patterns of AlSi10Mg and Al.

Size distribution is the other main factor that governs the reactivity of the fuel particles. The particles size measurement shown in Figure 4.3 provides a good insight into the statistical results of the dimensions of the material. As seen in the curve, only a tiny fraction of the particles is larger than 20 μm , which agrees well with the SEM images. Most particles have a diameter ranging from 8 to 18 μm . There is a tail under 8 μm in the curve, showing the existence of a quite significant number of particles with diameter of a few microns, corresponding to the smaller particles seen in SEM images. The D50 of the sample is found to be 13.1 μm . 50% of particles are below 13.1 μm . Therefore, 10 μm Al

particles are chosen as the reference sample to evaluate the performance of the AlSi10Mg as a metal fuel.

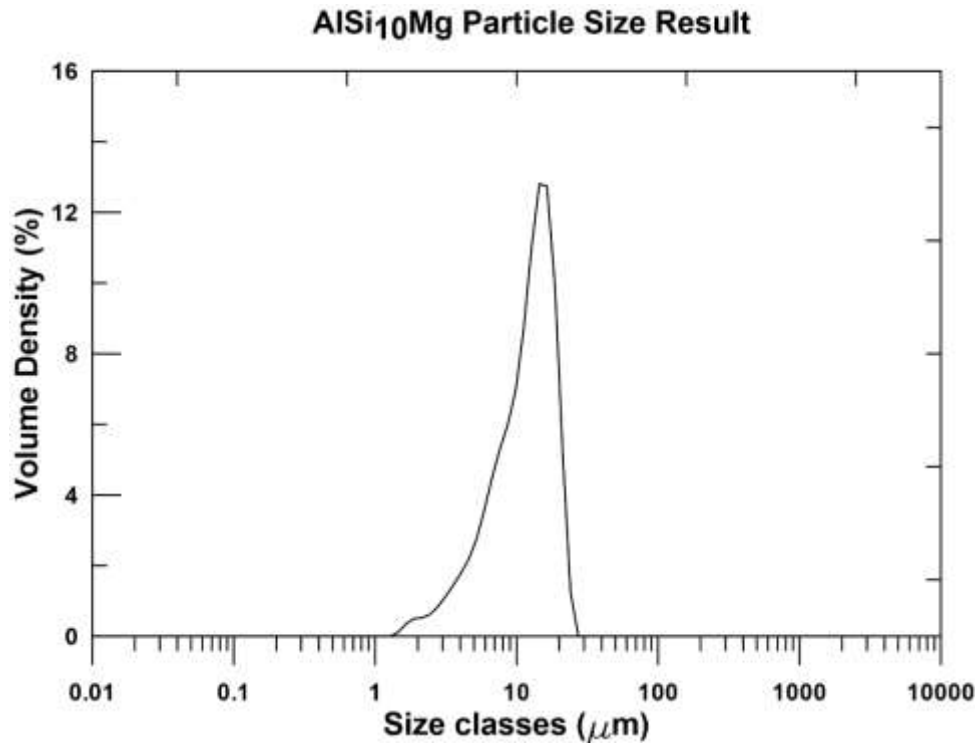


Figure 4.3 The AlSi10Mg Particle size analysis result.

Table 4 AlSi10Mg particle size analysis result

	Dv (10)	Dv (50)	Dv (90)
size distribution	5.35 μm	13.1 μm	20.2 μm

4.2 Reaction Mechanism of AlSi10Mg and Al

The DSC-TGA test is carried out to determine the thermal potential, the energetic performance of the alloy and its comparison with Al particles. Key parameters, including

the onset temperature, peak temperature, and energy release in each reaction, serve to analyze the energetic reaction pathway and composite structure.

Figure 4.4 presents the reaction of AlSi10Mg and Al with gaseous oxygen, with both AlSi10Mg and Al showing a similar pattern. In the DSC curve in Figure 4.4 a, an endothermal peak is found at 575 °C for AlSi10Mg, and 660 °C for Al, indicating the melting of the two materials. Due to the formation of alloy with the addition of Si and Mg, the melting point of AlSi10Mg is significantly reduced compared to pure Al. The first and only significant exothermic peak in the DSC curve for AlSi10Mg and micro-Al is observed just above 1000 °C. It initiates at 920.2°C for AlSi10Mg and 988.6°C for Al, reaching its peak at 1064 °C for AlSi10Mg and 1068.5 °C for Al. In the exothermal reaction, AlSi10Mg releases 11504 J/g of heat, which is four times greater than the heat released by Al (4182J/g). Moreover, AlSi10Mg presents a slightly lower onset temperature and peak temperature but higher heat release, indicating a longer-lasting reaction that may be caused by particles with slightly different reactivity in the sample, possibly as the result of the wider size distribution.

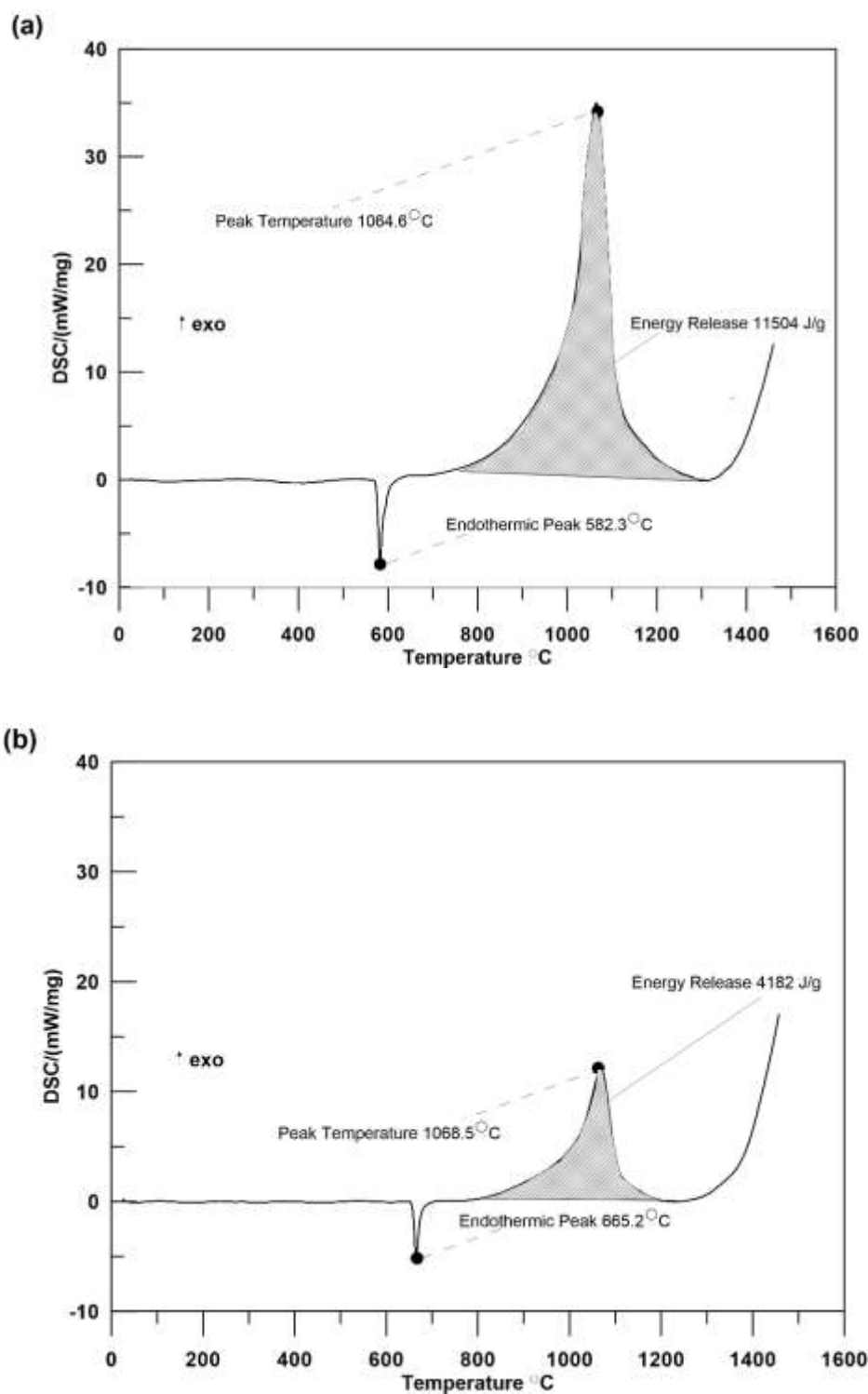


Figure 4.4 AlSi10Mg and Al in mixed N₂-O₂ environment at 20°C/min. (a) AlSi10Mg, (b) Micro-size Al (10 μm),

The Figure 4.5 shows the TGA and DTG results for AlSi10Mg and micron Al. Weight gain is also evident during the major exothermal reaction, with ~30% increase for AlSi10Mg and ~10% increase for Al, respectively. The weight gain is caused by the oxidation process, turning metal fuel into metal oxide. A theoretical weight gain should be around 100% for both AlSi10Mg and Al when all reductive metals are oxidized. Therefore, only a minor part of the fuel is oxidized during this first exothermic reaction, especially for pure Al. Correspondingly, the AlSi10Mg sample exhibits a substantially greater heat release upon exposure to oxygen around 1000°C. It indicates that AlSi10Mg may possibly present a higher reactivity than the 10- μ m Al particles, especially at lower temperatures, due to its ease of being oxidized around 1000 °C. As the temperature further increases, a second exothermal reaction peak and weight gain emerge, starting at around 1300°C, suggesting the further oxidation of the unreacted fuel once the temperature is high enough to increase the diffusivity of fuel and oxygen to trigger the reaction. However, the temperature limitation of the DSC-TGA instrument prevents us from determining the total energy release upon oxidation for both AlSi10Mg and Al.

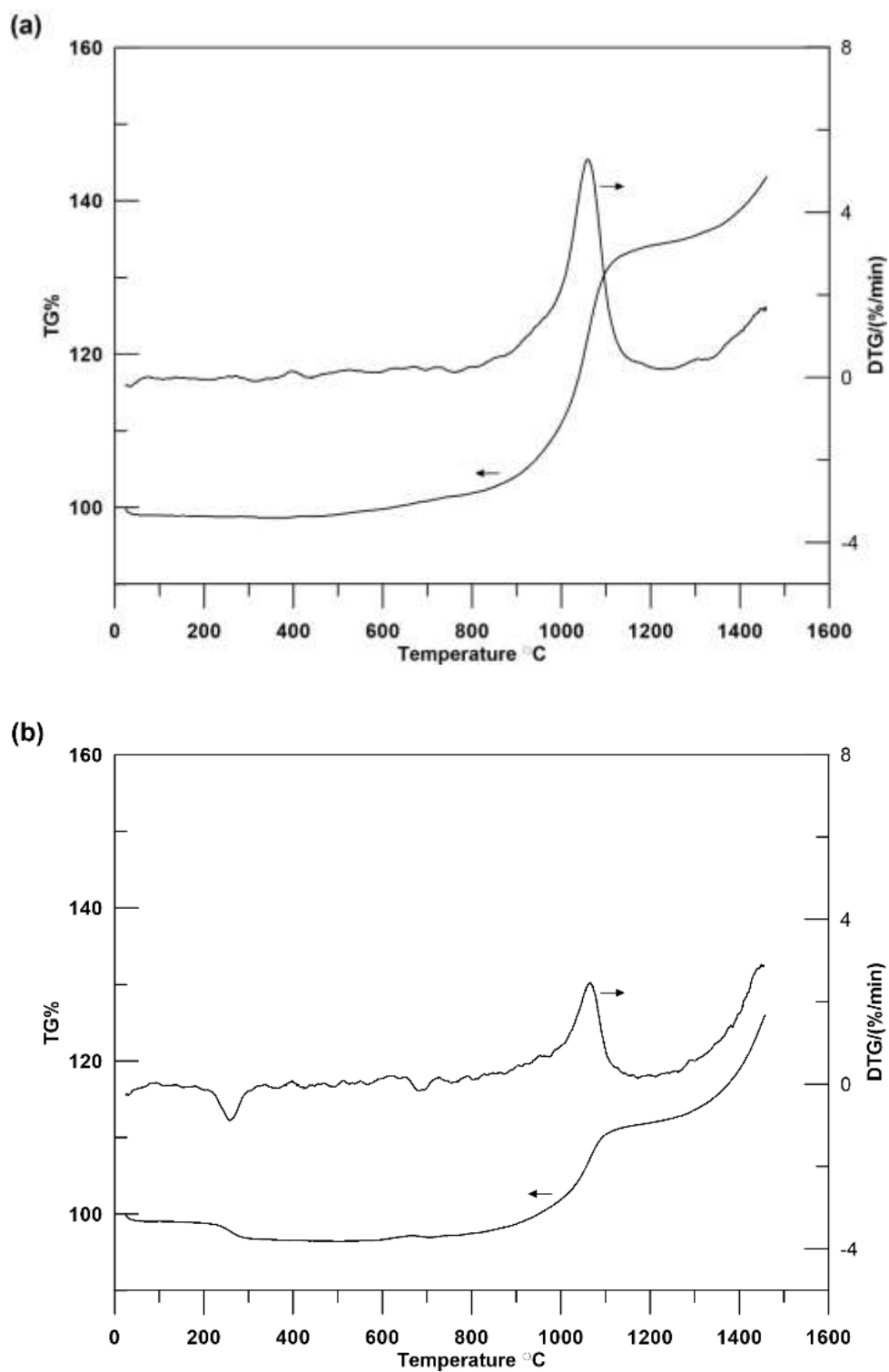


Figure 4.5 TGA and DTG of AlSi10Mg and Al in mixed N_2 - O_2 environment at $20^\circ\text{C}/\text{min}$.
(a) AlSi10Mg, (b) Micro-size Al ($10\ \mu\text{m}$)

In Figure 4.6, the DSC and TGA curves show an unclear increase at 1100 °C. It is speculated that the weight increase and second exothermal reaction may be that the metal (fuel) is not completely consumed, and the remaining metal fuel continuously reacts with oxygen. The metal sample must be continuously heated until the metal fuel is completely consumed. However, it is impossible to heat the sample above 1500 degrees due to the instrument's limited heating capabilities. So, the verification test can only be maintained at 1500°C for 30 minutes to ensure all the metal fuel is consumed.

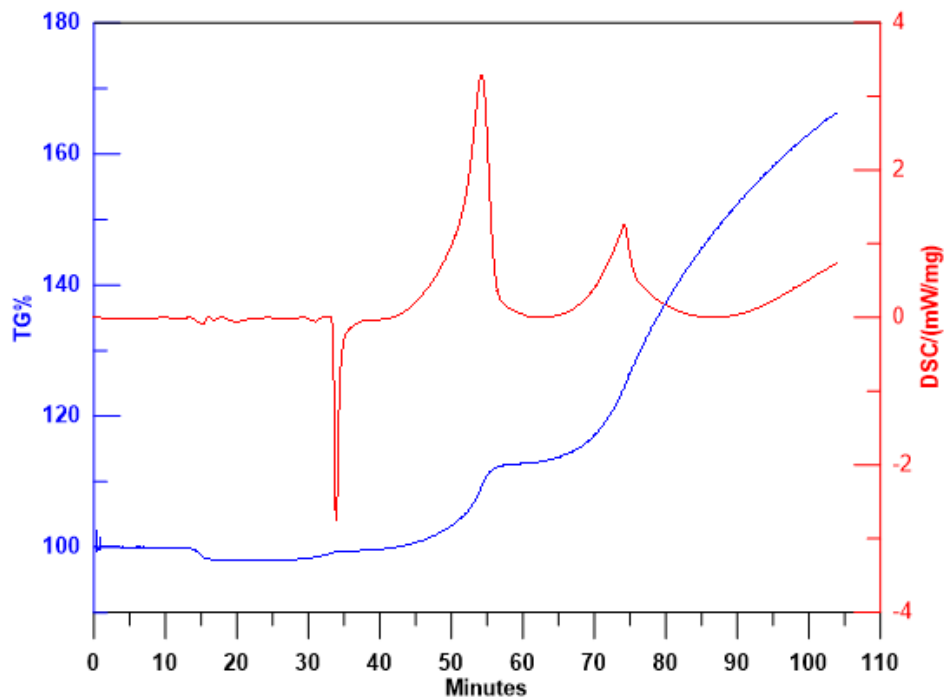


Figure 4.6 Micro-size Al in mixed N₂-O₂ environment for 104 minutes heating time

Figure 4.6 shows the result of the verification test. As predicted before, the rise of the DSC-TGA curve is because of incomplete consumption of the metal fuel. At 74 minutes, the DSC pattern starts to decrease and gradually slows down and the TGA pattern keeps rising after 60 minutes.

4.3 Activation Energy

Activation energy (E_a) represents the minimum energy to overcome the energy barrier to trigger the reaction, and it is a great indicator towards reactivity. Higher activation energy represents the requirement of a greater amount of energy to allow the occurrence of the reaction, usually leading to longer ignition delay and slower reaction rate in the thermite combustion. The Kissinger equation is used to calculate the activation energy, as shown in Equation 13.

$$\ln \frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \ln \left(\frac{AR}{E_a} \right) \quad \text{Equation 13}$$

where β represents the heating rate, T_p is the peak temperature, E_a indicates the activation energy, R and A represent the universal gas constant and pre-exponential, respectively. A series of DSC-TGA runs with different heating rates are usually coupled with Kissinger equation to determine the activation energy of a reaction. In this case, the Kissinger equation can be regarded as a liner function between $\frac{1}{T_p}$ and $\ln \left(\frac{\beta}{T_p^2} \right)$, where E_a can be determined as the slope of the fitted curve.

Five distinct heating rates at 10K/min, 15K/min, 20K/min, 25K/min and 30K/min are adopted to determine the peak temperature for each test in DSC, as the results shown in Figure 5. The activation energy of the first peak of oxidation of aluminum alloy

(AlSi10Mg) is 316.908kJ/mole and the activation of the first peak of oxidation of aluminum is 318.482kJ/mole.

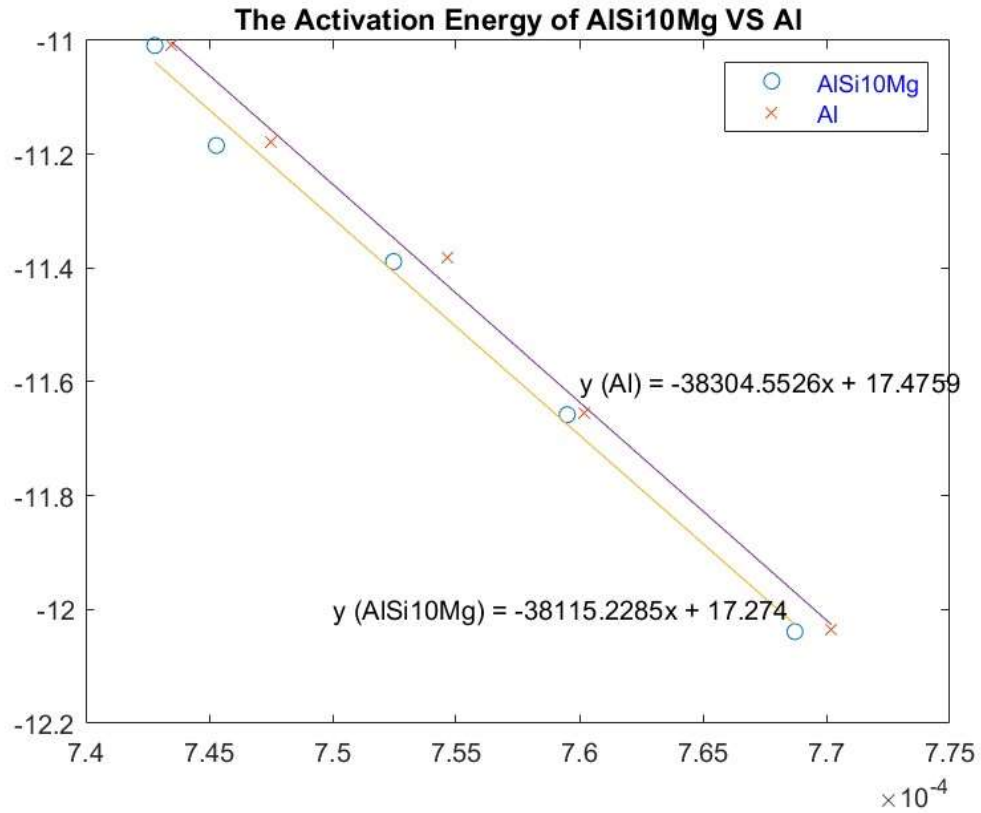


Figure 4.7 The Activation Energy of AlSi10Mg and Al

Table 5 Reaction mechanism for AlSi10Mg and micron-level aluminum

	Onset Temperature	Temperature with the max heat flow	Energy Release (J/g)	Mass Change	Activation Energy (kJ/mole)
AlSi10Mg	920.2°C	1064.6°C	11504	35%	316.908
Micro-Al	988.6°C	1068.5°C	4182	13%	318.482

The comparable activation energy and the DSC curves indicate a similar reaction pathway and reactivity between AlSi10Mg and Al. A high-temperature way above the melting point of both AlSi10Mg and Al is required to trigger the oxidation with gaseous oxygen, indicating the reaction is happening between the liquid-phase free-flow fuel and gaseous oxygen. However, only a small part of the fuel is oxidized during the first peak. The particle size plays a critical role in the oxidation reaction mechanism. For nano-sized Al particles, it is well known that condense-phase reaction occurs even before the melting of Al, caused by the crystallization of the amorphous Al_2O_3 shell and the increased diffusion as temperature ramps up, leading to a rapid while almost complete oxidation before the melting of Al. However, due to the large particle size of AlSi10Mg and micron-Al used here, the produced Al_2O_3 , SiO_2 and MgO formed a substantially thick shell, acting as a barrier on the surface of the particles, preventing the fuel from being further oxidized. It is hypothesized that the higher oxidation percentage of AlSi10Mg could be caused by the existence of the smaller particles, as well as a less dense shell due to the presence of SiO_2 and MgO instead of pure Al_2O_3 .

4.4 Reaction Mechanisms of CuO Oxidizer

The AlSi10Mg or the micron-sized aluminum reacts with CuO, resulting in an exothermic reaction. Investigating the reaction mechanism of CuO can be a reference for analyzing the reaction mechanism of thermite. The 0.5-micron CuO gradually increases from room temperature to 1500°C at a heat rate of 20K/minute. A minor endothermic peak appears on the DSC curve and a corresponding 10% weight loss is evident on the TGA curve at approximately 839°C, indicating the CuO decomposition into Cu₂O and O₂. As the temperature continued to rise, a massive endothermic peak occurs at around 1234°C, indicating the melting of the Cu₂O.

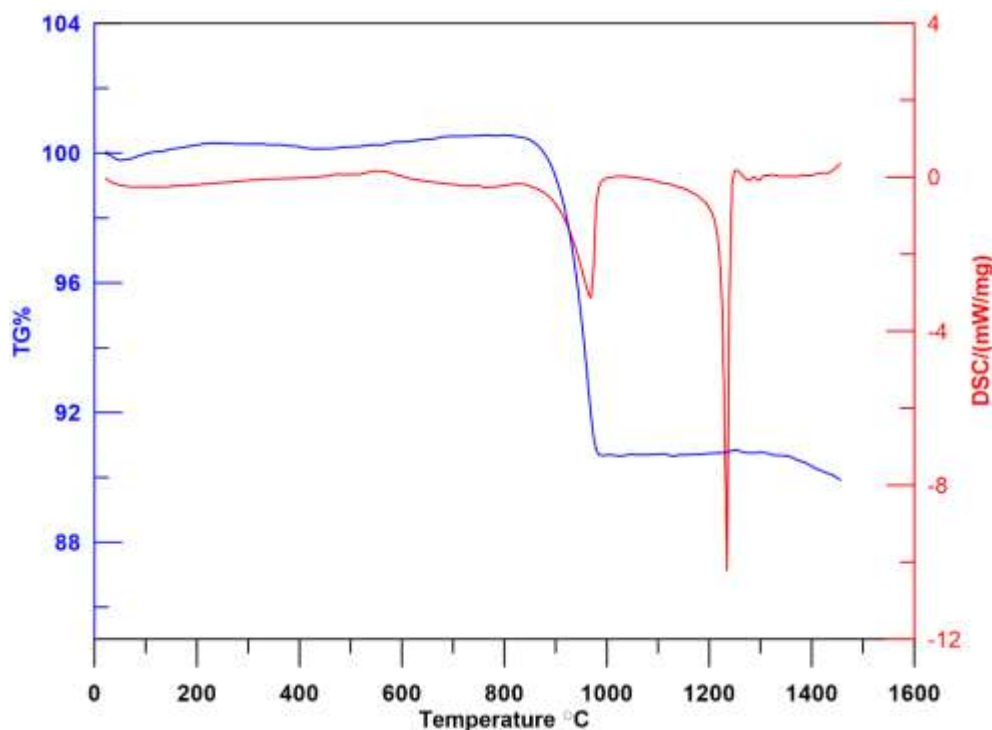


Figure 4.8 DSC and TGA result of CuO

4.5 The Reaction Mechanism of Solid Oxygen and Gaseous Oxygen

The reaction with oxygen gas reveals the theoretical energetic performance of AlSi10Mg and Al as fuel. However, supplying gaseous oxygen directly to react with fuel proves to be very challenging in real-world applications. Packing solid fuel as an energy supplying cell while eliminating its access to environmental oxygen is critical to understand its practical potential, such as propellant in space. Therefore, AlSi10Mg and Al are mixed with metal oxide to figure out their reaction. CuO and Fe₂O₃ are selected as two types of metal oxide to react with AlSi10Mg and micron-Al for DSC-TGA measurements under the protection of argon, as shown in Figure 4.9. Without the presence of environmental oxygen, the dissimilarity in reaction mechanism shows up.

The CuO decomposes to Cu₂O and O₂ around 900 °C, which is lower than the reaction temperature between AlSi10Mg / micron-Al and gaseous O₂. Therefore, an interesting fact is seen in Figure 4.9 a and b. After the endothermal peak from the melting of AlSi10Mg (575 °C) and Al (660 °C), no distinct exothermal peak is seen. Instead, a significant weight loss is seen in both samples around 900 °C due to the decomposition of CuO, accompanying an endothermal peak. A small exothermal peak is then shown right after the endothermal reaction around 1000°C, caused by the reaction between AlSi10Mg / micron-Al with the decomposed O₂ from CuO. As the temperature continues to increase, the reaction between 1000 to 1350°C is likely due to the reaction between AlSi10Mg/Al with solid and liquid (after 1235 °C) Cu₂O from the decomposition of CuO. Melting peaks of copper (1085°C) are also seen in both curves. Therefore, in the DSC-TGA test

of AlSi10Mg/CuO and Al/CuO, there exists multiple reactions, including liquid-gas, liquid-solid, and liquid-liquid reaction.

However, the reaction between the fuel with Fe_2O_3 is completely different. Due to the much higher decomposition temperature of Fe_2O_3 , the formation of gaseous O_2 is negligible during the heating process of the measurement, as confirmed by the absence of weight loss in TGA results. Therefore, a dominant exothermal reaction peak is shown for both AlSi10Mg/ Fe_2O_3 and Al/ Fe_2O_3 around 1100 °C, indicating a condensed phase solid-solid reaction between fuel and oxidizer. The reaction temperature here is much higher than the reaction temperature of the solid fuel with gaseous O_2 , indicating that diffusivity of oxidizer makes a great deal in terms of the reactivity of the final thermite mixture using micron-sized Al-based metal fuel due to the limited surface area to trigger the oxidation.

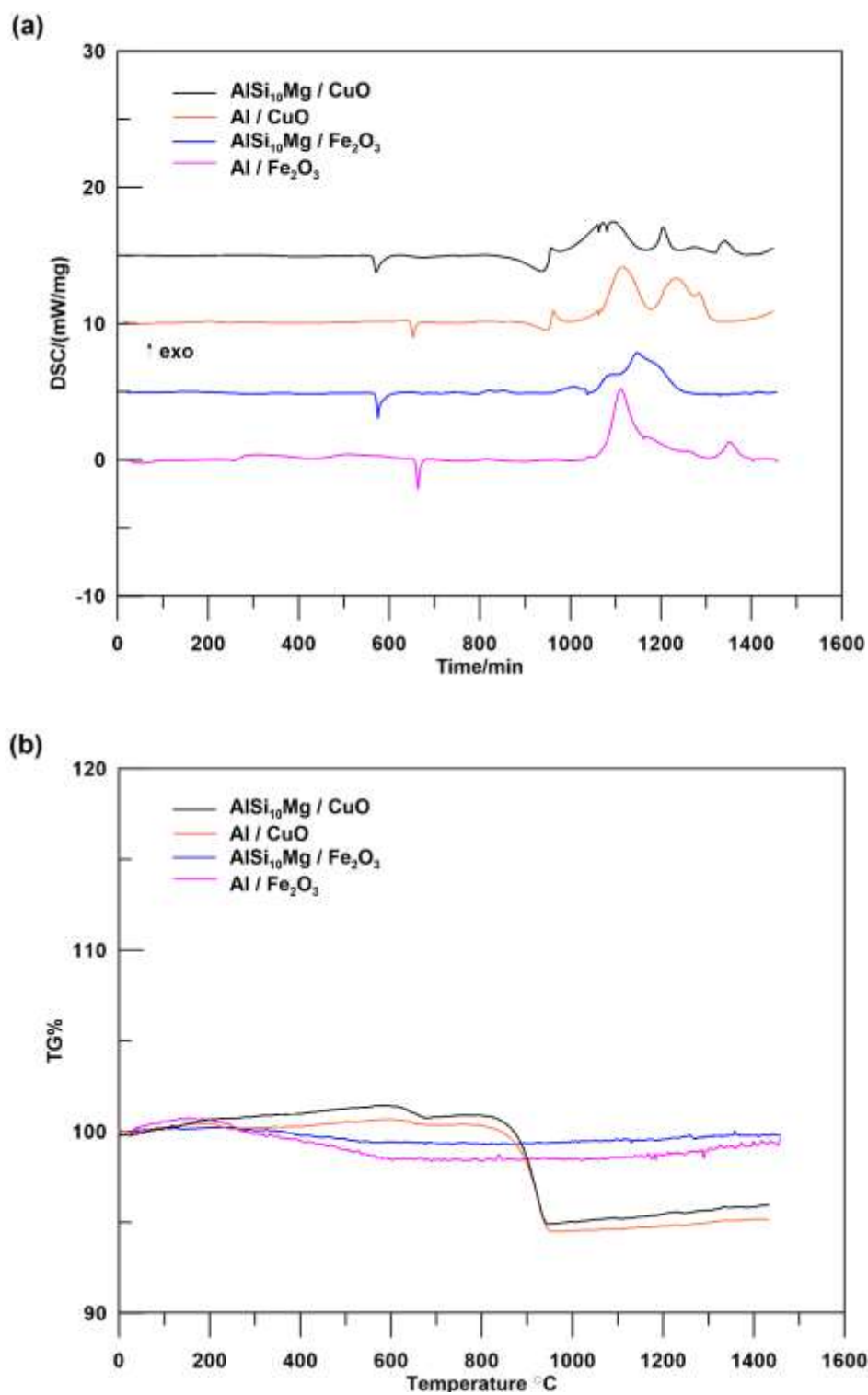


Figure 4.9 DSC and TGA result of AlSi10Mg/CuO, AlSi10Mg/ Fe₂O₃, Al/CuO and Al/ Fe₂O₃ (a) DSC (b) TGA

4.6 The Reaction Mechanism of AlSi10Mg/CuO and Al/CuO with Different ERs

The DSC measurements are then carried out for AlSi10Mg/CuO and Al /CuO with different ERs, as shown in Figure 4.10. All curves show very similar pattern, as discussed above. The direct reaction between fuel and oxidizer is basically non-existent due to the equilibrium environment in DSC-TGA, allowing the reaction to occur strictly following the order of temperature. The major reaction in DSC-TGA is found between fuel and Cu₂O after the decomposition of CuO and the subsequent liquid-gas reaction.

In both AlSi10Mg/Cu₂O and Al/Cu₂O, the first exothermic peak indicates reactions between liquid fuel and solid Cu₂O. The major difference between AlSi10Mg/Cu₂O and Al/Cu₂O are the temperature ranges of the reaction and minor reactions before and during the energetic reactions. For Al/Cu₂O, the first exothermic reaction ranges from 1100°C to 1200°C. Only one extremely minor melting peak is seen within the peak at 1085°C, indicating the melting of Cu, which can be generated by Al/CuO or Al/Cu₂O reaction at lower temperatures. The production of Cu is very limited. However, in AlSi10Mg/Cu₂O, the first exothermic reaction has a much earlier initiation around 1000°C, right after the decomposition of Cu₂O. Two tiny endothermic peaks are hidden within the prominent exothermic peak at 1070°C and 1085°C, indicating the melting of a possibly formed Al-Cu alloy and pure Cu after reduction by fuel. The melting peaks are also much more evident, confirming the significant Al-Cu alloy and Cu formation in the reactions. Therefore, AlSi10Mg has a boosted reactivity than Al with Cu₂O at lower temperatures. Considering that the temperature is much higher than the melting point of both fuels, particle size no longer plays a significant role here, and the increased reactivity is likely

caused by the addition of Si and Mg. After the first exothermal reaction, Cu_2O reaches its melting point at 1230°C , and the reaction occurs between melting fuel and melted oxidizer.

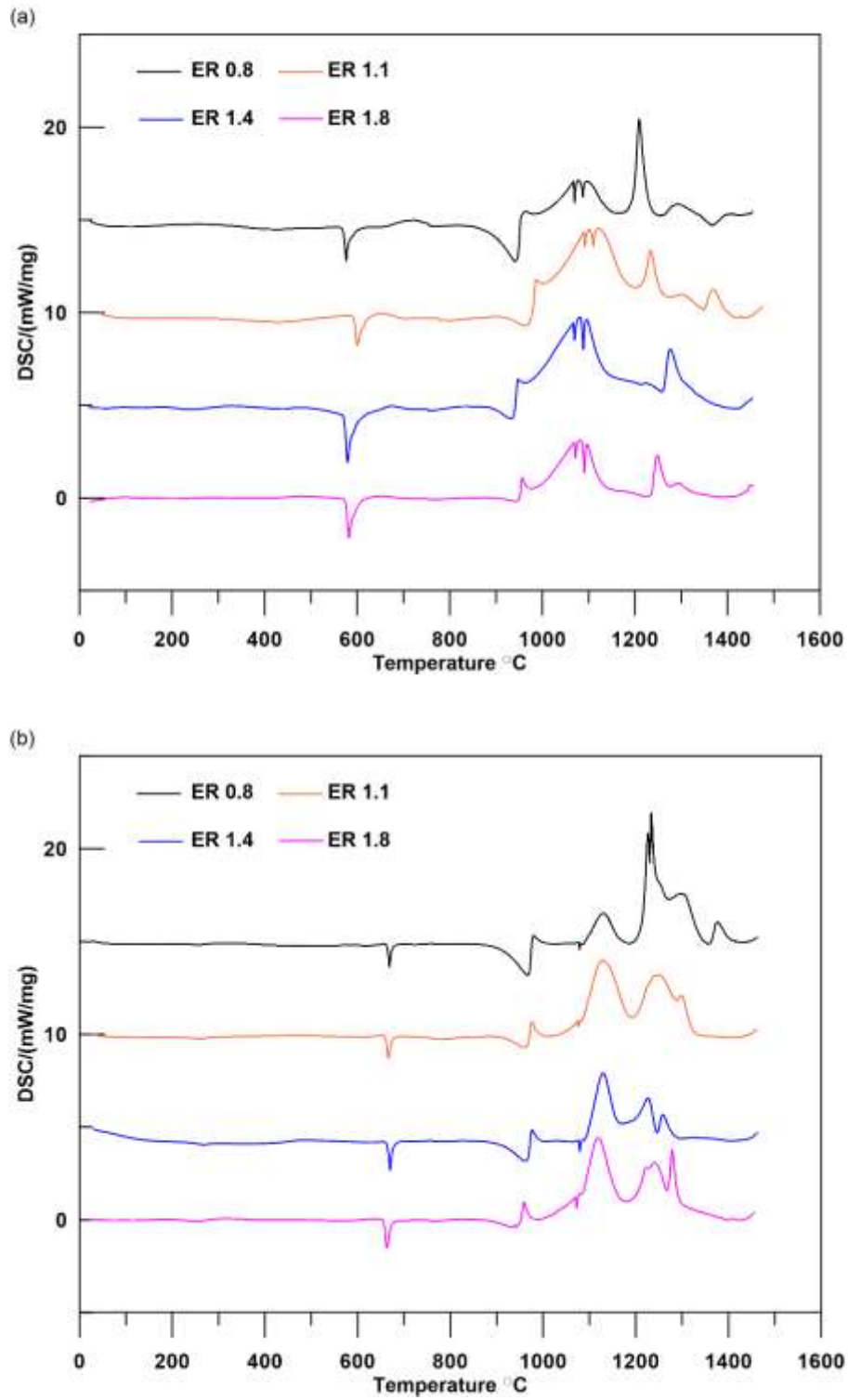


Figure 4.10 The DSC results with different ER (a) AlSi10Mg/CuO, (b) Al/CuO

4.7 Combustion Performance

Even though TGA-DSC results reveal that AlSi10Mg can be as reactive as micro-sized Al, the combustion performance remains ambiguous due to the complex interplay of heat and mass transfer during the process. Therefore, multiple combustion tests of AlSi10Mg/CuO and Al/CuO are conducted under atmosphere and vacuum.

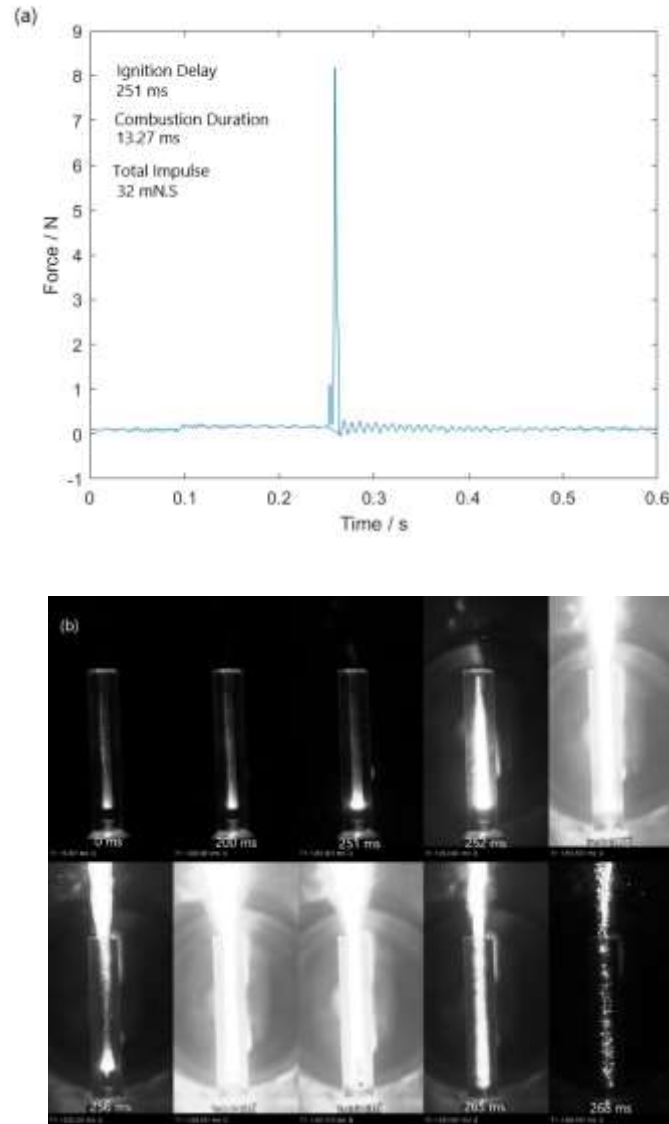


Figure 4.11 Key frames from the combustion video of AlSi10Mg/CuO (a) force response (b) a typical combustion video of AlSi10Mg/CuO.

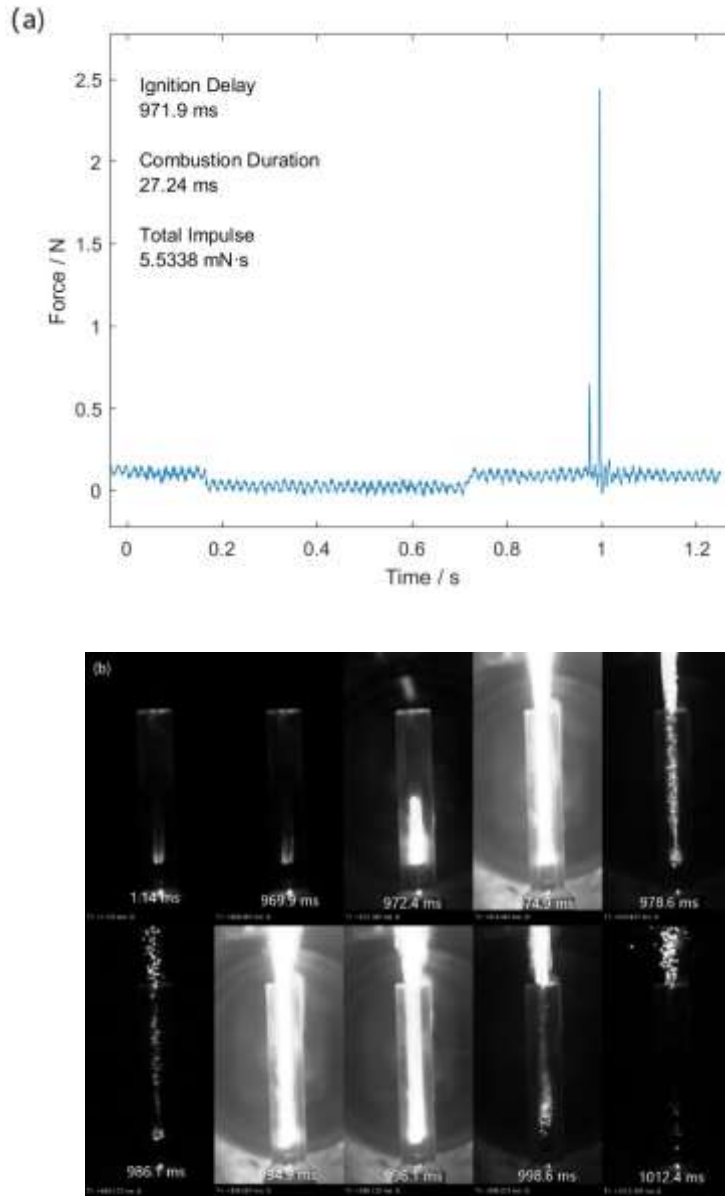


Figure 4.12 Key frames from the combustion video of Al/CuO (a) force response (b) a typical combustion video of Al/CuO.

Keyframes from the video and the corresponding force response collected from the force transducer of typical combustion are shown in Figure 4.11 and Figure 4.12. A laser beam

is shined from the top to heat the sample for ignition. The analysis of combustion primarily focuses on three parameters: ignition delay (energy required to trigger a self-sustainable reaction), combustion duration (rate of combustion propagation across the entire sample), and output impulse (violence of combustion). Time 0 is set to the time when the laser is turned on. The time gap after which pressure generation commenced is considered the ignition delay, and the duration of the pressure curve peak in the pressure plot corresponds to the combustion duration. In the test, AlSi10Mg/ Fe₂O₃, and Al/Fe₂O₃, are very difficult to ignite, indicating that the condense-phase reaction is not sufficient to support a self-sustainable combustion of the mixture due to its lower reaction rate compared to the gas-solid reaction. The released gaseous oxygen from CuO is the critical point that promotes the propagation of combustion.

For most AlSi10Mg/CuO and Al/ CuO samples, ignition delay times are hundreds of milliseconds, and combustion durations are tens of milliseconds. Before the combustion propagation, the reaction mainly happens on the surface of the sample, between fuel with oxygen from the environment or the decomposition of CuO. A multiple-stage combustion is shown in some samples during the combustion, as seen in Figure 4.11 and Figure 4.12. The first ignition occurs between 251 to 254 ms, brightness and force increase rapidly.. However, the brightness and force decrease between 254 to 256 ms before increasing again after 258 ms. This unique phenomenon indicates a two-step reaction in the sample, which is also reported before for nanoscale Al/CuO physically mixed samples. Initially, the reaction occurs between fuel (AlSi10Mg and Al) with gaseous O₂, which can be either from the environment or from the decomposition of CuO. After the first-stage

reaction, enough energy is released to trigger the unheated bulk of the sample and propagate under the surface, entering the second stage of reaction throughout the sample. During the second stage, due to the much higher heating rate that can easily reach 10^6 K/s or higher, the decomposition of CuO and the participation of gaseous O₂ become unimportant. The reaction can occur between fuel and CuO before decomposing as a condensed phase reaction or between fuel and O₂/Cu₂O. However, the bulky reaction will not be triggered if there is not enough energy provided from the first-stage reaction between fuel and gaseous O₂. Therefore, our tests find that AlSi10Mg/ Fe₂O₃ and Al/ Fe₂O₃ are very difficult to ignite despite their dominant condensed phase reaction, as seen in DSC-TGA. The condensed phase reaction alone is insufficient to trigger such a self-sustainable combustion of the mixture due to its lower reaction rate than the gas-solid reaction. The released gaseous oxygen from CuO is the key point that initiates the propagation of combustion. Additionally, since this research mainly focuses on directly comparing AlSi10Mg and Al as solid fuel, the nozzle is not designed and applied to the exit of the tube. Therefore, the major contributor to the force recorded is the pressure drop as the heated gas, which is the atmosphere within the tube, escaped from the exit.

The following pictures show the critical combustion properties of AlSi10Mg/CuO and Al/CuO. The thermite fails to ignite at an equivalence ratio (ER) of 0.6. Thus, the results for ER 0.6 are not included in the plots.

4.7.1 Ignition Delay

The Figure 4.13 displays the ignition delay for the AlSi10Mg/CuO and Al/CuO. The ignition delay exhibits a clear trend that peaked at ER 1.1 and decreased with higher or lower ER, indicating a slightly more significant energy input is needed to trigger the combustion propagation at this equivalence ratio. Al/CuO presents significant uncertainty regarding ignition delay, indicating more randomness during its ignition. AlSi10Mg/CuO shows a shorter ignition delay than Al/CuO at most different equivalence ratios. The existence of smaller particles in the mixture contributes to the reduced ignition delay and less uncertainty of AlSi10Mg. Because the gaseous oxygen participates in the reaction, there is enough surface area to contact oxygen, which can be either from the environment or, more importantly, from the decomposition of CuO, which may escape from the mixture if not captured by fuel particles. Therefore, the smaller particles in AlSi10Mg play a significant role in arresting the gaseous oxygen from decomposition and thus accumulating the initiation energy required for self-sustainable combustion, leading to mostly shorter ignition delay and better consistency between tests.

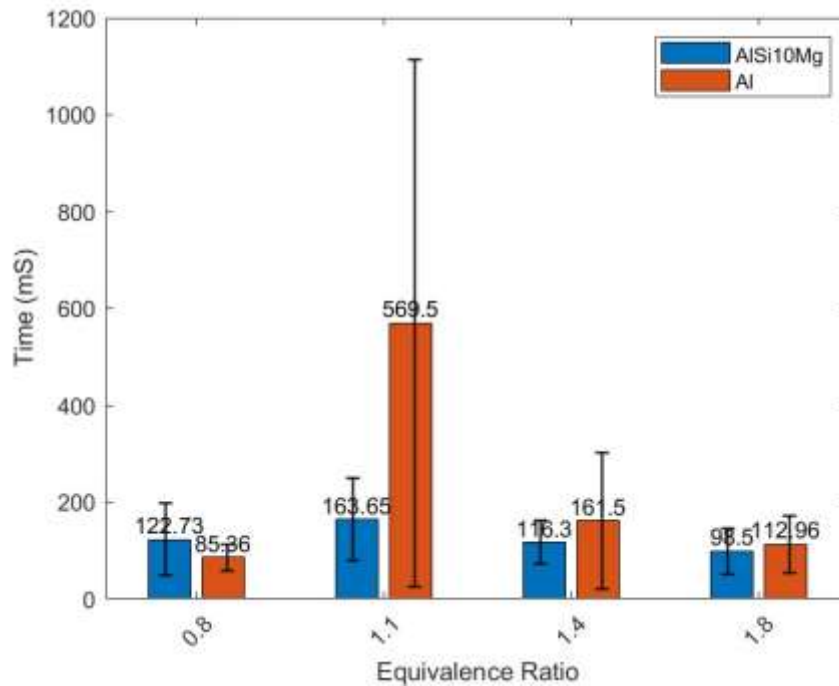


Figure 4.13 Ignition delay for AlSi10Mg/CuO and Al/CuO in atmosphere.

4.7.2 Combustion Duration

The following Figure 4.14 shows the combustion duration for AlSi10Mg/CuO and Al/CuO. Similar to the ignition delay results, the Al/CuO has the most extended ignition delay at ER 1.1, indicating the slowest ignition propagation among all samples. The Al/CuO samples of other ERs show a shorter combustion duration compared to the ER 1.1, but all are much longer than AlSi10Mg/CuO, which has a combustion duration between 11 – 16 ms. Like the ignition delay, the combustion duration is affected by the reactivity, which is determined by the composition and some physical factors. The addition of Si and Mg changed the propagation rate, and the smaller particles in AlSi10Mg also bring in some features similar to nanoparticles, leading to faster propagation.

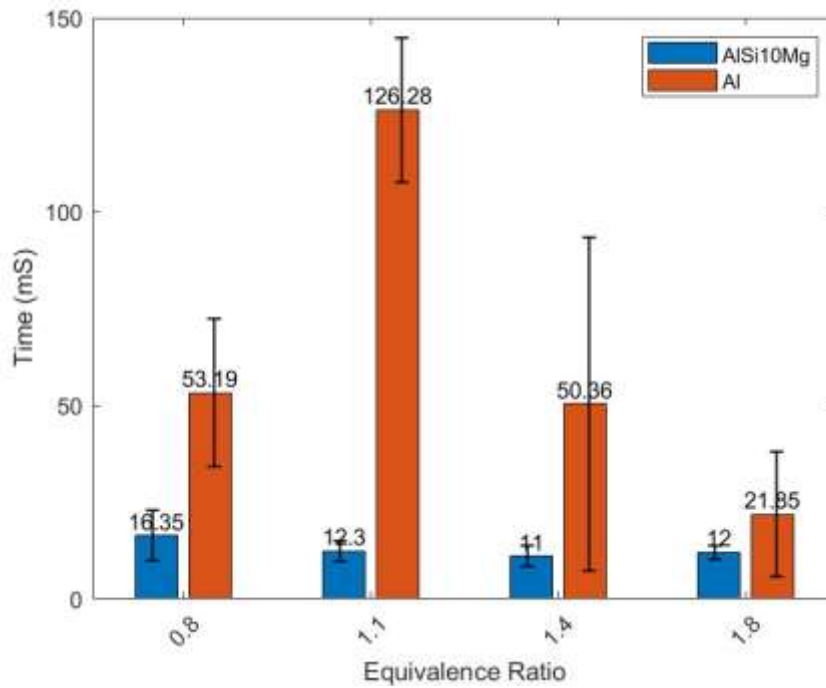


Figure 4.14 Combustion duration for AlSi10Mg/CuO and Al/CuO in atmosphere

4.7.3 Combustion Impulse

The Figure 4.15 shows the combustion Impulse for AlSi10Mg/CuO and Al/CuO. Regarding impulse output, Al/CuO and AlSi10Mg/CuO output the least force at ER 0.8 due to the fuel-lean condition. In fuel-rich conditions, however, the metal oxide can be effectively used, and some environmental oxygen can also participate in the combustion, leading to much more significant impulse output. AlSi10Mg/CuO generates a much more significant thrust than Al/CuO, even with a shorter combustion duration, indicating a much higher exit gas temperature during combustion, which is the critical contribution from metal fuel in solid propellant.

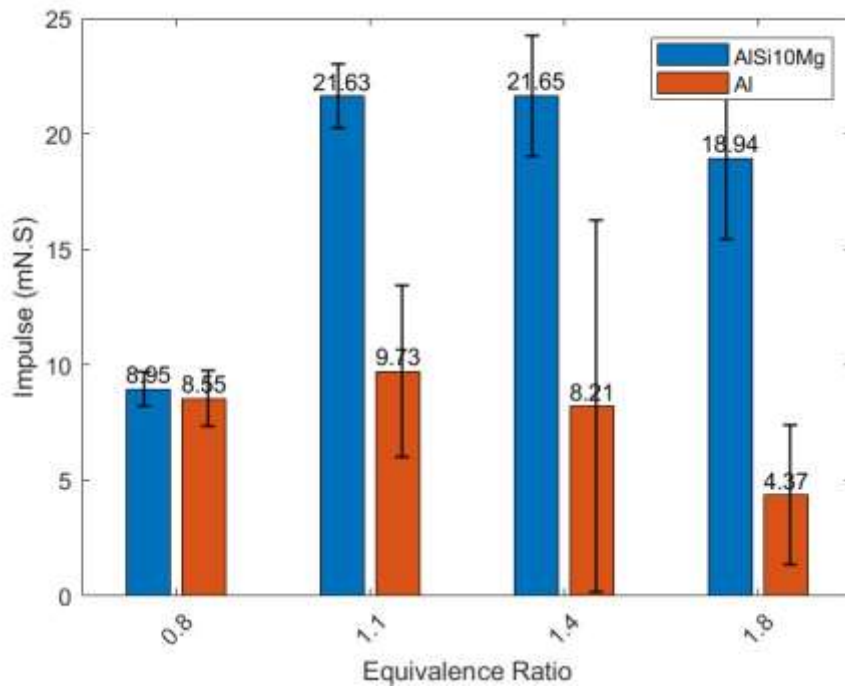


Figure 4.15 Combustion Impulse for AlSi10Mg/CuO and Al/CuO in atmosphere

4.7.4 Combustion in the Vacuum

Considering the possible application of the metal fuel as propellant under vacuum, conducting combustion under a low-pressure environment is necessary. In this case, gaseous oxygen from the environment is no longer available; thus, the gaseous oxygen released from the decomposition of CuO is the only source to trigger the reaction. However, in the vacuum environment, the decomposed oxygen can easily escape from the mixture. Therefore, the ability to capture oxygen to trigger the reaction is critical. The following Figure 4.16 shows the combustion process for AlSi10Mg/CuO under the vacuum. The ignition delay is around 1.5 seconds, much longer than the ignition delay observed in the air. The longer ligation delay is due to the lack of oxygen supply in the environment. The Al/CuO cannot be ignited under low pressure, while the AlSi10Mg/CuO can be ignited. The successful ignition of the AlSi10Mg in a vacuum

environment can prove that AlSi10Mg has higher reactivity than pure Al. During ignition, some particles or hot sparks are injected from the tube, which never occurs in air combustion. The absence of air leads to no pressure to bind the fire sparks during combustion. The absence of air leads to no pressure to bind the fire sparks during combustion so that fire sparks can be injected freely. Nevertheless, the impulse cannot be recorded due to the absence of an atmosphere, the expansion of which is the main contributor to the measurement.

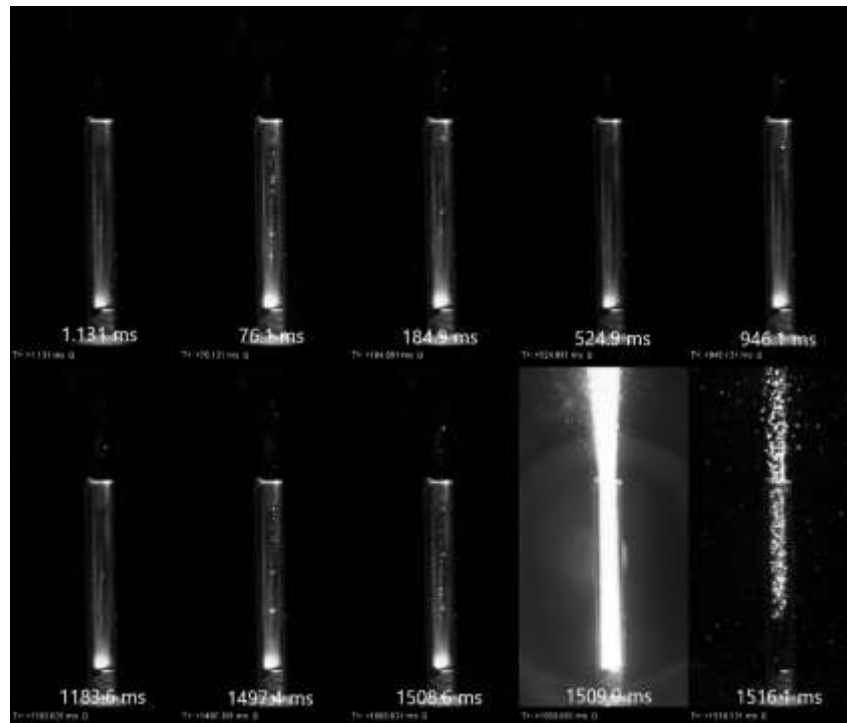


Figure 4.16 Key frames (a) and force response (b) from a typical combustion video of Al/CuO

5 Summary and Future work

5.1 Summary

This thesis investigates structural properties, energetic characteristics, and combustion performance of micro-sized industrial waste AlSi10Mg alloy particles, and their comparison to those of micro-sized Al particles. The microscopic and XRD measurements confirm the formation of metal-metal bonds and the size range of these AlSi10Mg particles. The SEM-EDS reveals the composition of the Al-based alloy to be 82% aluminum, 10% silicon and 1% magnesium. The DSC-TGA results under $\text{N}_2\text{-O}_2$ environment show a similar reaction temperature around 1000°C and a comparable activation energy with O_2 gas to that of pure Al particles. However, AlSi10Mg produces a higher energy release and a larger weight gain with gaseous O_2 at the low temperature, indicating its faster oxidation than micron-Al in that range. When reacting with metal oxide (CuO), the behavior of AlSi10Mg and micron-Al highly relies on the decomposition of metal oxide. During TGA/DSC where the alloy reacts with a metal oxide with a relatively high decomposition temperature, such as Fe_2O_3 , the onset temperature for the thermite reaction has been found to be $1100\sim 1200^\circ\text{C}$ which is much higher than those for the AlSi10Mg/ O_2 and Al/ O_2 reactions. However, when the alloy particles react with CuO, the onset temperature is lower and the reaction between fuel and oxidizer involves gaseous O_2 . Combustion tests confirm the importance of generating gaseous O_2 , which is critical to trigger combustion of the micro-sized reactive material. The mixtures of AlSi10Mg/ Fe_2O_3 and Al/ Fe_2O_3 cannot be easily ignited by laser due to less production of gaseous oxygen. A two-step reaction mechanism is proposed for both AlSi10Mg/CuO and Al/CuO thermites during the combustion tests. First, the initiation

occurs between the fuel and gaseous O_2 at the top surface of the sample. Then, energy from the surface reaction triggers the bulk reaction of the sample. Compared to micron-Al with a comparable average particle size, AlSi10Mg/CuO presents a better performance as a solid fuel in all different tests including a shorter ignition delay, a shorter combustion duration, and a higher impulse output. Moreover, the successful combustion of AlSi10Mg/CuO under vacuum affirms the possibility of using AlSi10Mg as a promising metal fuel in space environment compared to micro-sized Al, which cannot be ignited with CuO in vacuum. In summary, the AlSi10Mg powder from additive manufacturing industry has a great potential to be used as an alternative to micron-Al for heat and pressure generation, while reducing the industrial waste to generate an added value.

5.2 Future Work

More vacuum tests are needed to confirm if AlSi10Mg can supply sufficient power for propulsion. Additionally, the thrust test requires the installation of a nozzle, which is a diverging and converging device. The primary function of the nozzle is to evaluate the performance of AlSi10Mg/CuO solid propellant in practical applications. Nevertheless, it is difficult to monitor the force or impulse generated by AlSi10Mg/CuO in a vacuum environment due to the absence of atmosphere; some gas-generating fibers or nitrocellulose (NC) can be considered to be added into thermite.

Each metal species plays a distinct role in combustion. As mentioned earlier, magnesium (Mg) can increase reactivity and boron (B) offers a high specific calorific value. It is necessary to compare the different combustion performances of the most common metal

alloys and understand the corresponding properties of thermites. For example, Mg can be added to the thermite formulation to test the ignition (good for the application of car airbags).

The DSC-TGA of AlSi10Mg/CuO and Al/CuO displays multiple exothermal peaks after 1200°C. The reasons behind these exothermal peaks are not clear. There is a need to explain the reaction mechanisms of AlSi10Mg/CuO and Al/CuO after 1200°C. The XRD tests may be arranged to determine the composition and phases of these products related to each exothermal peak.

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