# **Experimental Study of Combustion Characteristics of Micron-Sized Aluminum Particles and Liquid Water**

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Experiments have been performed to explore the combustion behaviors of spherical micron-sized aluminum ( $\mu$ Al) particles and liquid water for Al particle sizes in the range of  $3.5-25 \ \mu m$ . The ignition of quasi-homogeneous  $\mu$ Al/water mixtures was successfully implemented by employing a novel ignition method, and self-sustained flame propagation was obtained in the mixtures over a broad range of fuel-equivalence ratio  $\phi$ . The burning rates, flammability limits, and thermal structure of the propagating flame were determined. The combustion products were also analyzed. For the particle sizes considered, the burning rates were found to first increase and then decrease as  $\phi$  increased, with the maximum values occurring at  $\phi = 1.7-2.0$  and substantially lower than nano-Al/H<sub>2</sub>O mixtures. The dependence of the burning rate on particle size follows a power law,  $r_b \sim D^{-0.18}$ , indicating that the reaction process of  $\mu$ Al and water is kinetically controlled. Base on the experimental observations, a simplified flame propagation model was developed to provide insight into the effects of particle size and equivalence ratio. Combustion product analyses revealed that Al residues increased as  $\phi$  was further increased from 0.7, and the combustion efficiency of aluminum decreased accordingly.

## Nomenclature

- specific heat capacity,  $J/(kg \cdot K)$ =
- = particle size,  $\mu m$
- = activation energy, kJ/mol
- coefficient =
- = constant
- pressure, MPa =
- = universal gas constant,  $J/(mol \cdot K)$
- = burning rate, mm/s
- = temperature, K
- = adiabatic flame temperature, K
- = ambient temperature, K
- $T_{\rm am}$ = measured flame temperature, K
  - = flame temperature field, K
  - = ignition temperature, K
  - = particle temperature, K
  - = water boiling temperature, K
  - = burning time, ms
  - = ignition time, ms
  - = thermal diffusivity, m<sup>2</sup>/s
- $\Delta T$ = temperature difference, K
  - = flame thickness, mm
  - = characteristic flame temperature
  - = thermal conductivity,  $W/(m \cdot K)$
  - = density, kg/m<sup>3</sup>
- φ = fuel-equivalence ratio

fuel-lean limit =  $\phi_{\text{lean}}$ fuel-rich limit =  $\phi_{\rm rich}$ 

# I. Introduction

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T HE combustion of aluminum particles and water provides a promising candidate for underwater propulsion [1-4] and space propulsion [5,6]. Aluminum/water mixtures are also of interest to hydrogen generation and fuel cell technology [7]. In the recent past, the combustion characteristics of nano-aluminum (nAl) in water have been extensively studied [5,8–11], because nAl is relatively easy to ignite due to its much higher specific surface area compared with micron-sized Al ( $\mu$ Al). Risha et al. [8,11] reported that the burning rate of nAl/H2O mixtures increases significantly with decreased particle size for a particle diameter range of 38-130 nm, and the mass burning rate increases from 1.0 to 5.8 g/( $cm^2 \cdot s$ ) for equivalence ratios between 0.5 and 1.25. They also found that the combustion efficiencies range from 27 to 99% depending on particle size and sample preparation (i.e., packing density). Sundaram et al. [9] experimentally and theoretically investigated the effects of pressure and particle size on the combustion behavior of stoichiometric nAl/H<sub>2</sub>O mixtures. For the particle size range of 38–130 nm and ambient pressure of 1-10 MPa, the correlation among the burning rate, pressure, and particle diameter was shown to have the form  $r_{b} \text{ [cm/s]} = 98.8 \times (P[\text{MPa}])^{0.32} (D[\mu\text{m}])^{-1.0}$ . In practical applications, frozen aluminum/water mixtures might be used as a solid propellant. Pourpoint et al. [12] tested the feasibility of using nAl/ ice (ALICE) propellant in a small rocket. The frozen mixtures were found to be stable, and insensitive to electrostatic discharge, shock, and impact. Risha et al. [13] performed steady-state solid rocket motor experiments fueled by 80 nm aluminum/ice mixtures. For a 7.62-cm-internal-diam combustion chamber, the ALICE propellant could produce thrust levels above 992 N with a combustion efficiency of 69% and a specific impulse efficiency of 64%. They also found that at a higher pressure (>8 MPa), the combustion efficiency was improved and the ignition became easier.

Used as fuel, however, the disadvantages of nAl are rather notable as compared with  $\mu$ Al [14]. Particularly, the great proportion of the oxide layer in nAl substantially reduces the energy density. For example, active aluminum only account for 54.3% of the total mass for particle size of 38 nm [8], whereas the active aluminum content is nearly 100% in micron-sized particles. In addition, the high reactivity of nAl has the side effect of spontaneous reaction when mixed with water. Micron-aluminum is therefore an even more desired fuel for practical applications, although it seems necessary to promote the

с

D

 $E_a$ K

 $K_1$ 

Р

R

 $r_b$ T

 $T_{ad}$ 

 $T_b$ 

 $T_f$ 

 $T_i$ 

 $T_p$ 

 $T_v$ 

 $t_b$ 

 $t_i$ 

α

δ

θ

λ

ρ

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combustion performance of  $\mu$ Al. Sundaram et al. [10] and Sundaram and Yang [15] conducted combustion experiments of  $\mu$ Al and liquid water by adding either nAl to reduce ignition temperature or hydrogen peroxide  $(H_2O_2)$  to enhance oxidant reactivity. With the addition of nAl or hydrogen peroxide, the  $\mu$ Al/water mixtures were successfully ignited; nevertheless, the burning rates decrease significantly when the loading density of each addition is decreased. Ki et al. [14] used flaky  $\mu$ Al powder for increasing specific surface area to ensure ignition and stable combustion of µAl/water mixtures, and measured the burning rates of flaky  $\mu$ Al with liquid water over a broad range of pressures, mixture compositions, and densities. The burning rate increases with the increase in pressure, and it strongly depends on equivalence ratio and density due to the thermal conductivity of the sample. As far as we know, however, there is no report on experimental works that ignite and burn up micron-sized spherical Al particles in water without adding combustion improver. This leads to an obvious lack of fundamental understanding of the combustion between  $\mu$ Al and water, and hinders its further application in propulsion engineering.

In this work, the self-sustained propagation of flame in spherical  $\mu$ Al and H<sub>2</sub>O mixtures is experimentally studied. The Al particle size ranges from 3.5 to 25  $\mu$ m, and the tested Al-H<sub>2</sub>O equivalence ratio covers the whole flammable range. Quasi-homogeneous mixtures of Al and H<sub>2</sub>O are successfully ignited by employing a novel ignition method, and stable combustion is achieved. The burning rates are measured for various particle sizes and equivalence ratios, and a simplified model based on the ignition and burning processes of single Al particle is constructed to interpret the effects of particle size and equivalence ratio on flame propagation. Elemental compositions and morphology of the reaction products are analyzed to provide further information on aluminum combustion efficiency. The present results provide basic data on the combustion of micron Al and water, in which no combustion improver is used, and expand the physical understanding of  $\mu$ Al-H<sub>2</sub>O combustion processes.

## II. Experimental

A schematic of the experimental setup is shown in Fig. 1. The combustion experiments were conducted in a 26 L cylindrical constant volume chamber equipped with gas, electrical signal, electrical power, and optical viewing ports. The chamber could be operated



Fig. 1 Schematic diagram of the experimental apparatus.



Fig. 3 Particle size distribution of the Al powders.

over a pressure range from vacuum to 3 atm, and the chamber pressure was monitored continuously by a transducer during the tests. Before each test, the combustion chamber was exhausted before filling it with argon (99.999% pure) to reach a pressure of 1.1 atm. The exhausting and filling procedure was repeated for three times, and finally a vent valve on the chamber was opened manually to balance pressure inside the chamber and ambient. Thus, the present experiments were conducted in argon at an initial pressure of 1 atm. During all tests, the pressure rise caused by the release of gaseous combustion products and heat was relatively small, with the maximum pressure less than 1.3 atm.

Commercially available micron-sized Al powders (99.7% pure, Yuanyang Co., Ltd.) were used. The Al particles had a median diameter (D = D50) of 3.5, 6.5, 10, 18, and 25  $\mu$ m, respectively. Scanning electron microscopy (SEM) images for three powders are shown in Fig. 2, illustrating the good sphericity and smooth surface of the particles. The particle size distributions in Fig. 3, measured by a Mastersizer 2000 Laser Particle Size Analyzer (LPSA) with water used as the dispersant, show a compact Gaussian shape. The span values (= [D90 - D10]/D50) are less than 1.1. The 3.5  $\mu$ m Al particles have an average specific surface area of 1.89 m<sup>2</sup>/g, which is 7.68 times larger than that of 25  $\mu$ m Al. To prevent the settling of  $\mu$ Al particles and obtain quasi-homogeneous  $\mu$ Al/H<sub>2</sub>O mixtures, 2 wt% polyacrylamide (average molecular weight  $1.2 \times 10^7$ , Macklin, Inc.) was added as gellant to 98 wt% distilled water, and the resulting gel was then mixed with Al powder in desired proportion. The prepared  $\mu Al/H_2O$  mixtures were loaded into an ash-free filter paper shell tube having a length of 60 mm and a diameter of 16 mm. The mixture sample was ignited at the top of the tube using specially designed ignition method. The ignition charge had two major components: the top layer was made up of 69% ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) and 31% magnesium powder (Mg), whereas the bottom layer consisted of a stoichiometric  $\mu$ Al/H<sub>2</sub>O mixture. A DC power supply was applied to an embedded nichrome wire in the  $Fe_2O_3/Mg$ layer, and the heated electrical wire then energized the ignition charge layer by layer. Temperature inside in the  $\mu$ Al/H<sub>2</sub>O mixtures was measured by a type-C thermocouple (thickness 75  $\mu$ m, W-5%Re/W-26%Re, Omega Engineering, Inc.) located at the midpoint of the test sample, with a data collection frequency of 100 Hz. The thermocouple measurement uncertainty is  $\pm 4.5$  °C at  $0 \sim 425^{\circ}$ C and  $\pm 1\%$  at  $426 \sim 1750^{\circ}$ C. A digital video camera was



Fig. 2 SEM images of the Al powders used: a)  $D = 3.5 \,\mu\text{m}$ ; b)  $D = 10 \,\mu\text{m}$ ; c)  $D = 25 \,\mu\text{m}$ .

used to record the combustion process through the perspective window.

After each test, the combustion product was collected. A Coxem Em-30 SEM and a Rigaku SmartLab 9 KW X-Ray Diffractometer (XRD) were employed, respectively, to analyze the morphology and compositions of the reaction product.

# III. Results and Discussion

# A. Flame Propagation and Flammability Limits

In the current experiments, the flammability limit of  $\mu Al/H_2O$ mixtures has been defined as the limiting mixture composition for quasi-steady flame propagation throughout the test sample. Both lean and rich limits could be readily determined with such a definition, although they may be subjected to the influence of ignition scheme and sample configuration. The fuel-lean and fuel-rich limits, represented by fuel-equivalence ratio  $\phi$ , are summarized in Table 1 for the five particle sizes. Overall, a wide flammable range is seen for the  $\mu$ Al/H<sub>2</sub>O mixtures. The lean limit  $\phi_{\text{lean}}$  increases slightly from 0.50 to 0.65 and the rich limit  $\phi_{\rm rich}$  decreases from 2.70 to 2.30 as the particle size increases from 3.5 to 25  $\mu$ m, clearly indicating the decreased flammability of large Al particles in liquid water. For all the  $\mu$ Al particle sizes investigated, the apparent limit equivalence ratios seem random to some degree. This observation can be partially explained by the inherent instability of near-limit flame propagation. In Table 1, the lean limits were determined as the minimum equivalence ratio where the flame was observed to propagate stably, and the rich ones as the maximum equivalence ratio, whereas the actual limits in repeated tests could occur at 0.05 higher or 0.05 lower equivalence ratios for lean and rich flames, respectively. Considering the wide flammable range, however, the measurement uncertainty of flammability limits is small. More important is that the reported flammability limit data provide a critical measure of the  $\mu$ Al/H<sub>2</sub>O mixtures' overall combustibility.

Within the flammable range, i.e., when  $\phi_{\text{lean}} \leq \phi \leq \phi_{\text{rich}}$ , selfsustained flame propagation can be obtained in  $\mu$ Al/H<sub>2</sub>O mixtures. Figure 4 presents video images of the flame propagation process in

Table 1 Fuel-equivalence ratios at lean and rich flammability limits of the  $\mu$ Al/H<sub>2</sub>O mixtures

Particle diameter, µm	Lean limit	Rich limit
3.5	0.50	2.70
6.5	0.60	2.50
10	0.55	2.50
18	0.55	2.30
25	0.65	2.30



Fig. 4 Images of flame propagation in stoichiometric  $10 \ \mu m \ Al/H_2O$  mixture. The time interval between images is 8 s.



Fig. 5 Flame front position as a function of time for  $10 \ \mu m \ Al/H_2O$  mixtures with different equivalence ratios.

the stoichiometric 10  $\mu$ m Al/H<sub>2</sub>O mixture. As shown, a luminous front propagates downward until the sample bottom is reached. The flame grows dim over time due to the generated oxide smoke and ash particles that are carried into the field of view by the hydrogen and steam release. By tracking the flame propagation processes, which were recorded for all flammable mixtures, the velocities of flame propagation can be derived. To avoid the influence of ignition and flame extinction, the middle burning part of the test sample is analyzed for this purpose. In addition, three representative locations along the transverse direction of the sample (i.e., midpoint, and two locations that are 4 mm away from the lateral boundaries, respectively) are chosen to track the position of the flame leading front, because the flame generally develops a nonuniform shape. Figure 5 shows the time evolution of the averaged flame front position in 10  $\mu$ m Al/H<sub>2</sub>O mixtures with different  $\phi$ . Steady flame propagation is indicated by the linear variation of position with time, and the slope of each line represents a constant propagation velocity.

Using the constant flame velocity, the measured time-dependent temperature can be transformed into a spatial temperature profile of the propagating flame in Al/H<sub>2</sub>O mixtures. Figure 6 shows such a typical temperature profile for stoichiometric 10 µmAl/H<sub>2</sub>O mixture, and five zones have been identified according to the temperature gradient. The distance origin is chosen as the boundary between zone A and zone B, where liquid water gasifies. Generally, in zones A-C the mixture of Al and water is persistently heated up by conduction from the reacting particles, whereas the combustion reaction of Al particles takes place in zone D. Zone A and zone B are divided by the water boiling point temperature (373 K). When the vaporization of liquid water is completed, the Al/H<sub>2</sub>O mixture would enter zone B, which is characterized by a sharp temperature rise. The transition from zone B to C occurs at  $T \approx 920$  K, where pure aluminum content in the Al particles begins to melt. The melting may lead to the fracture of the oxide film at its weakest point, but the cracks can then be healed up by the reaction of exposed liquid aluminum with water vapor [16]. The process of cracks generation and repair continues until the



Fig. 6 Spatial temperature profile of the propagating flame in stoichiometric 10  $\mu$ m Al/H<sub>2</sub>O mixture.

ignition occurs [17]. The consumed heat for Al melting would make the temperature rise to slow down, whereas the partial reaction of exposed molten aluminum with water vapor will release heat [18]. Such combined effects result in a deceleration in the temperature rise after the melting point. The observed Al melting point is in good agreement with the measured value (933 K) by Schoenitz et al. [19] for 3–4.5  $\mu$ m Al powder in steam. Zone D is entered at  $T \approx 1395$  K, where Al particles ignite and the temperature gradient increases. Because intense exothermic reaction takes place in this zone, the temperature increases until Al particles burn out. Gurevich et al. [20] determined experimentally that the ignition point of 20  $\mu$ m Al particles in water vapor medium is 1300 K, consistent with the present observation. Zone E, the postcombustion zone, has an essentially constant temperature  $T_b \approx 1920$  K, which is obviously lower than the calculated adiabatic flame temperature  $T_{\rm ad} \approx 2856$  K, but approximates the flame temperature (1960 K) of stoichiometric 8.5  $\mu$ m (mean volume diameter) Al powder and H<sub>2</sub>O mixture measured by Narayana Swamy and Shafirovich [21]. The present flame temperature is also similar to the measured value (1800 K) for the stoichiometric 100 nm Al/H<sub>2</sub>O mixture [22].

The temperature profile in Fig. 6, when compared with the thermal structure of homogeneous premixed-gas flames, is characterized by a concave shape near the ignition point of Al particles. It is interesting to note that the concave temperature distribution may be a general feature of metal/water flames. For instance, Muraleedharan et al. [23] have proposed a similar flame temperature profile for nAl/H<sub>2</sub>O mixtures that taken the effects of Al phase transition and ignition into account. Temperature profiles of the propagating flame in Mg/H<sub>2</sub>O mixtures, as determined experimentally by Diwan et al. [24], showed a similar concave feature at the ignition temperature of Mg powder, although its metal phase transition process seemed not so obvious as the present  $\mu$ Al/H<sub>2</sub>O flames because of the lower ignition point of Mg than its melting point.

The adiabatic flame temperatures in Al/H<sub>2</sub>O mixtures,  $T_{ad}$ , are calculated using the NASA chemical equilibrium applications (CEA) program [25]. In Fig. 7,  $T_{ad}$  is shown as a function of equivalence ratio, together with the measured flame temperature  $T_b$  for 10  $\mu$ m Al at  $\phi = 0.7, 1.0, 1.4, 1.7, and 2.0$ . The adiabatic temperature reaches a peak value (2856 K) at  $\phi = 1.0$ , and decreases with the increased or decreased equivalence ratio. There are two temperature plateaus at 2327 K corresponding to the melting point of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) [7,8], which are caused by the enthalpy of Al<sub>2</sub>O<sub>3</sub> melting. The difference between  $T_b$  and  $T_{ad}$  is notable, with  $T_b$  is always lower than  $T_{ad}$  and a maximum discrepancy approximately of 865 K occurs at  $\phi = 1.0$ . The lower flame temperature in experiments may be induced by inevitable radiative heat loss from the flame. Also note that the measured flame temperature is less sensitive to equivalence ratio than the theoretical value does.

#### B. Burning Rate

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Figure 8 shows the measured burning rate (flame propagation velocity),  $r_b$ , as a function of equivalence ratio for the 3.5-, 6.5-,



Fig. 7 Adiabatic flame temperature  $T_{ad}$ , measured flame temperature  $T_b$  (for 10  $\mu$ m Al), and temperature difference  $\Delta T$  at different equivalence ratios.

10-, 18-, and 25-µm-diam Al/H<sub>2</sub>O mixtures. Each data point is the average of three repeated tests, and the standard deviation varies from 3.5 to 7.2%. The uncertainties may be caused by compounding errors in mixture ratio, irregular flame front, and flame front position reading. For all the particle sizes, the burning rate first increases and then decreases as  $\phi$  increases. The maximum burning rates are observed at  $\phi \approx 1.7-2.0$ , which take 2.32, 2.00, 1.85, 1.97, and 1.96 mm/s for the 3.5, 6.5, 10, 18, and 25  $\mu$ m particles, respectively. For a given equivalence ratio, as expected, the burning rate is consistently increased when Al particle size decreases. The present  $\mu$ Al/H<sub>2</sub>O burning rate is substantially lower than nAl/H2O mixtures, for which the burning rates predicted by Sundaram et al.'s empirical correlation [9] at 0.1 MPa reach up to 18.1, 6.41, and 3.64 mm/s for stoichiometric 38, 80, and 130 nm Al/H<sub>2</sub>O mixtures, respectively. As a comparison, the burning rates experimentally determined by Ki et al. [14] for 0.5  $\mu$ m × 30  $\mu$ m × 30  $\mu$ m flake Al powder and liquid water mixtures are also plotted in Fig. 8, and they have a similar magnitude to the present 3.5  $\mu$ m Al/H<sub>2</sub>O mixtures. Regardless of the difference in Al particle shape, the burning rate shows the same non-monotonic trend with respect to  $\phi$ , whereas for the flake  $\mu$ Al the rich flammability limit is extended.

Figure 9 shows the burning rate as a function of particle diameter for stoichiometric  $\mu$ Al/H<sub>2</sub>O mixtures. The dependence of the present burning rate on particle size appears to follow a  $D^{-0.18}$  law, which is close to the experimental findings ( $r_b \sim D^{-0.13}$ ) of Sundaram et al. [10] and Huang et al. [17] for kinetically controlled reaction of Al and water. In contrast, for nAl/water mixtures, Risha et al. [8] reported a  $D^{-1}$  dependence of the burning rate, and considered the reaction as diffusion-controlled according to the combustion synthesis analysis of Tomasi and Munir [26].

Based on the ignition and burning processes of a single Al particle, a simplified model for flame propagation in Al/H2O mixtures can be developed to explore the effects of particle size and equivalence ratio. The analysis describes one-dimensional, steady flame propagation as a result of Al particle ignition in an approaching flame. As illustrated in Fig. 10a, for simplicity, a linear temperature field ranging from water boiling temperature  $(T_v)$  to adiabatic combustion temperature  $(T_{ad})$  is used to characterize the thermal behavior of the flame. In the coordinate system attached to the propagating flame, the assumed flame structure can be depicted as an equivalence time-dependent one (Fig. 10b), and an Al particle enters the flame temperature field  $(T_f)$ with the burning rate  $r_b$  of the mixture. The particle is then heated up rapidly until ignition occurs at  $t_i$  as its temperature  $T_p$  reaches the ignition temperature  $T_i$ , and the ignited metal keeps burning for a time interval  $t_b$  in the reaction zone. Thus, the burning rate is determined by  $r_b = \delta/(t_i + t_b)$ , where  $\delta$  is the flame thickness that covers the preheat zone and reaction zone. Generally  $\delta$  is expressed as  $\delta \sim \alpha/r_b$ , in which  $\alpha$  is the thermal diffusivity of the unburned Al/H2O mixture, so a further expression can be achieved,  $r_b \sim [\alpha/(t_i + t_b)]^{1/2}$ , which correlates the burning rate of a bulk Al/H<sub>2</sub>O mixture to the ignition and burning times of a single Al particle. Here note that a single temperature profile is employed to describe the overall flame and the solid phase; i.e., the particle thermal relaxation is neglected. Other model assumptions include uniform particle size and particle temperature, and constant ambient pressure.

The burning time of an Al particle depends primarily on its initial size, the ambient temperature, and the oxidizing atmosphere [15,17,27,28]. For a kinetically controlled reaction, it was derived by Huang et al. [17] that

$$t_b = \frac{K_1 D^{0.3}}{e^{-E_a/RT_{\rm am}} \cdot X_{\rm eff}} \tag{1}$$

where  $K_1$  is a constant equaling  $1.147 \times 10^{-3}$ , *D* the particle diameter in  $\mu$ m,  $E_a = 73.6$  kJ/mol the activation energy, R = 8.314 J/ (mol · K) the universal gas constant,  $T_{\rm am}$  the ambient temperature, and  $X_{\rm eff} = X_{\rm O_2} + 0.6X_{\rm H_2O} + 0.22X_{\rm CO_2}$  the effective oxidizer mole fraction, and  $t_b$  has a unit ms.



Fig. 8 Measured burning rate as a function of equivalence ratio for different µAl and the flake Al powder results of Ref. [14].



Fig. 9 Burning rate of stoichiometric  $\mu Al/H_2O$  mixtures as a function of particle size.

For a moving aluminum particle in the specified temperature field of Fig. 10b, the neglect of particle relaxation allows an estimate of the ignition time as

$$t_i = \frac{T_i - T_v}{T_{\rm ad} - T_i} t_b \tag{2}$$

Recall that  $r_b \sim [\alpha/(t_i + t_b)]^{1/2}$ , and by substituting Eqs. (1) and (2), the burning rate is

$$r_b \sim \sqrt{K\alpha(1-\theta^{-1})} \cdot D^{-0.15} \tag{3}$$

where  $K = e^{-E_a/RT_{am}} \cdot X_{eff}/K_1$ , and  $\theta = (T_{ad} - T_v)/(T_i - T_v)$ . The obtained expression demonstrates clearly the dependence of the burning rate on the Al particle diameter *D*, the characteristic flame temperature  $\theta$ , and the thermal diffusivity of Al/H<sub>2</sub>O mixture  $[\alpha = \lambda/(\rho c)]$ , where  $\lambda, \rho$ , and *c* are thermal conductivity, density, and



Fig. 10 Schematic diagrams of the spatial flame structure in Al/H<sub>2</sub>O mixtures (a) and physical model of Al particle ignition and burning in the flameattached coordinate (b).

specific heat capacity, respectively. In particular, the relationship  $r_b \sim D^{-0.15}$  is consistent with the present experimental result of  $r_b \sim D^{-0.18}$  and previous experimental result of  $r_b \sim D^{-0.13}$  [17]. The value of  $(1 - \theta^{-1})$  may be primarily affected by the equivalence ratio, and when  $\phi$  increases its variation trend is similar to that of the flame temperature as shown in Fig. 7. The thermal conductivity of Al/H<sub>2</sub>O mixture ( $\lambda$ ) is estimated by solving the Maxwell–Eucken–Bruggeman (MEB) model [15,29], and the density  $\rho$  and specific heat capacity *c* are calculated with the weighted average. The thermal



Fig. 11 XRD patterns for combustion products of the  $10 \ \mu m \ Al/H_2O$  mixtures with equivalence ratio of 0.55, 1.0, and 1.4.

diffusivity  $[\alpha = \lambda/(\rho c)]$  is then determined to increase significantly from 0.25 to 1.69 mm<sup>2</sup>/s as  $\phi$  increases from 0.5 to 3.0. Consequently, for fuel-lean mixtures  $r_b$  increases with the increasing  $\phi$ since  $\alpha$  and  $(1 - \theta^{-1})$  both increase. For fuel-rich mixtures, however,  $\alpha$  increases but  $(1 - \theta^{-1})$  decreases with  $\phi$ , and so  $r_b$  is determined by the competing effects of increased thermal conduction and reduced flame temperature, and a peak value may occur at an equivalence ratio greater than unity.

### C. Combustion Product Analyses

Figure 11 presents the measured XRD spectra for postcombustion products of the 10  $\mu$ m Al/H<sub>2</sub>O mixtures with different equivalence ratios ( $\phi = 0.55$ , 1.0, and 1.4). Almost only aluminum oxide peaks appear at  $\phi = 0.55$ , indicating that the reaction of Al and water is nearly complete. The XRD spectra for  $\phi = 1.0$  and 1.4, however, show both aluminum and aluminum oxide peaks to denote the incomplete combustion of Al. Additionally, at  $\phi = 1.4$  the Al peaks become more intense and Al residues in the combustion product are further increased.

Figure 12 shows the SEM micrographs for the product remains of the same 10  $\mu$ m Al/H<sub>2</sub>O mixture samples. At  $\phi = 0.55$ , the alumina product appears as irregular agglomerates. When the equivalence ratio is increased to 1.0, individual spheroidal particles and round bulges on the agglomerates can be observed, which have a diameter of approximately 10  $\mu$ m and may be molten but unburned aluminum. At  $\phi = 1.4$ , the molten Al particles seem to increase in the combustion product, and they could agglomerate together to form larger clusters.

The mass proportions of Al<sub>2</sub>O<sub>3</sub> and Al in the combustion products are determined from XRD analyses. The combustion efficiency of aluminum,  $\eta$ , herein defined as the mass ratio of consumed portion to total aluminum content in the sample mixture, can then be obtained. The results for the 10  $\mu$ m Al/H<sub>2</sub>O mixtures are shown in Fig. 13 as a function of equivalence ratio. Under ultra-lean reaction conditions, i.e.,  $\phi \leq 0.7$ , the Al mass content in the combustion products could be



Fig. 12 SEM micrographs for combustion products of the 10  $\mu$ m Al/H<sub>2</sub>O mixtures.



Fig. 13 Combustion product compositions and combustion efficiency of Al ( $\eta$ ) for the 10  $\mu$ m Al/H<sub>2</sub>O mixtures.

6% at most and the corresponding combustion efficiency reaches at least 0.9. Furthermore, the product compositions and the combustion efficiency show little change for these fuel-lean mixtures. When the equivalence ratio is further increased, more and more residual Al is present in the combustion product, and the combustion efficiency decreases gradually. To be specific,  $\eta$  decreases to a value of 0.78 at  $\phi = 1.0$ , and at  $\phi = 1.8$  it is as low as 0.49. In theory, the combustion efficiency of Al in water should be 1 when  $\phi \leq 1.0$ , and decreases with the further increase of equivalence ratio. The experimental results of  $\eta$  appear to follow the same trend of the theoretical anticipation (shown as the dashed line in Fig. 13), but the actual combustion efficiency of Al is lower.

## IV. Conclusions

The combustion of spherical micron-sized aluminum and liquid water was investigated experimentally for Al particle sizes in the range of  $3.5-25 \ \mu$ m. Without the use of any combustion improver, the following were determined: burning rates, flammability limits, and thermal structure of the propagating flame. A simplified flame propagation model was developed to provide insight into combined effects of particle size and fuel-equivalence ratio; the combustion products were also analyzed.

The ignition of quasi-homogeneous mixtures of spherical  $\mu$ Al particles and liquid water was successfully implemented, and selfsustained flame propagation was obtained in the mixtures over a broad range of equivalence ratios, showing that the  $\mu$ Al/H<sub>2</sub>O mixtures' flammable range becomes narrower to some degree as the Al particle size increases. Within the flammable range, for the particle sizes considered, the burning rates first increase and then decrease as  $\phi$  increases, with the maximum values occurring at  $\phi = 1.7$ –2.0 and substantially lower than nAl/H<sub>2</sub>O mixtures.

The particle size dependence of the burning rate follows the power law  $r_b \sim D^{-0.18}$ , indicating that the reaction process of  $\mu$ Al and water is kinetically controlled. Experimental data show that the temperature profile of the propagating flame in  $\mu$ Al/H<sub>2</sub>O mixtures is characterized by a concave shape near the ignition point of Al particles. The simplified flame propagation model, which was based on Al particle ignition and burning in an assumed linear temperature field, however, can capture essentially the dependence of the burning rate on both particle size and equivalence ratio. Al residues were found to increase in the combustion products as the equivalence ratio was further increased from 0.7, and the combustion efficiency of aluminum decreases accordingly.

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