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Effects of particle size and pressure on combustion of nano-aluminum particles and liquid water

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ABSTRACT

The combustion wave propagation of nanoaluminum–water mixtures is studied theoretically and experimentally for particles in the size range of 38–130 nm and over a pressure range of 1–10 MPa. A multi-zone framework is established to predict the burning properties and flame structure by solving the conservation equations in each zone and enforcing the mass and energy continuities at the interfacial boundaries. The flame properties are measured by burning nanoaluminum–water strands in a constant-volume vessel. The present study deals with the downward propagating flame. Emphasis is placed on the effects of particle size and pressure. An analytical expression for the burning rate is derived, and physicochemical parameters that dictate the flame behavior are identified. For conditions present in the study, the burning rate shows pressure and particle size dependencies of the form r_b [cm/s] = $98.8 \times (p$ [MPa]$)^{0.32}(d_p$ [nm]$)^{-1.0}$. The flame thickness increases with increasing particle size and decreasing pressure. Results support the hypothesis that the combustion of aluminum–water mixtures is controlled by mass diffusion across the oxide layers of the particles.

1. Introduction

The combustion of aluminum particles in water is of relevance to many propulsion and energy-conversion applications. In metalized composite solid propellants, aluminum particles typically react with the combustion products of the polymeric binder and ammonium perchlorate, of which water vapor (H_2O) and carbon dioxide (CO_2) are two major species [1]. The problem is of particular interest for underwater propulsion, since the oxidizer (water) could be supplied from the environment [2]. The combustion of aluminum particles in water has also been studied in the contexts of hydrogen generation [3], nuclear reactor and industrial manufacturing safety [4], and underwater explosives [5]. The frozen mixture of aluminum particles and water (ALICE) is also under consideration for several energetic applications, due to its structural integrity [6,7].

The ignition and combustion characteristics of aluminum particles in water are different from those in oxygenated environments. Figure 1 shows the effect of pressure on the aluminum vaporization temperature ($T_{v,Al}$) and adiabatic flame temperature (T_f) of aluminum–water mixtures with different particle sizes and water in various thermodynamic states. The particles are assumed to be passivated, with an oxide shell thickness of 3 nm. The flame temperature is lower than the vaporization temperature for pressures over a "cut-off" value. For micron-sized particles, this occurs in the range of ~1–4 atm, depending on the thermodynamic state of water. For nano-sized particles, the cut-off pressure is as low as ~0.2 atm. This can be attributed to the fact that the inert oxide layer constitutes a greater portion of the particle mass at nanoscales; a 50 nm aluminum particle, for example, contains 32 wt.% oxide [5]. It should be pointed out that the actual flame temperature can be lower than the theoretical value, due to the effects of heat losses and incomplete combustion. As a result, in most practical cases, nano-aluminum does not vaporize and heterogeneous chemical reactions occur at the particle surface.

Figure 2 shows the effect of particle size on the ignition temperature of aluminum particles in water–vapor containing environments. Oxidation was studied by various methods including a thermogravimetric analyzer [8], electrical heating [9], shock tube [10], hydrogen–oxygen–argon burner [11], and arc burner [12]. Both spherical particles [8,10–12] and wire samples [9] were considered. In the thermo-gravimetric experiments [8], the particles were heated at relatively low rates in the range of 1–20 K/min. The oxidizing gas consisted of 27% H_2O and 73% Ar. The reactions were observed at much lower temperatures in water vapor than in oxygen. Specifically, a stepwise weight change was observed at the melting point of aluminum (660 °C) and the particle is completely oxidized at ~1000 °C. Note that the experimental conditions are different in the referenced studies. For example, the

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Nomenclature

C_p	specific heat
d_p	particle diameter
h_{fg}	enthalpy of water vaporization
k	velocity-to-thermal diffusivity ratio
M	mass
p	pressure
Q_r	heat of reaction
r	core radius
R	particle radius
r_b	burning rate
t	time
T	temperature
v	velocity
x	spatial coordinate
y	normalized spatial coordinate

Greek

ρ	density
δ_f	flame thickness
δ_v	water vapor zone thickness
α	thermal diffusivity
η	normalized particle diameter
θ	normalized temperature
κ	normalized burning rate
λ	thermal conductivity
μ	normalized heat release
τ_b	burning time
Φ	volume fraction

Subscript

0	reference/initial state
b	burn
f	flame, fluid
G	gaseous reaction zone
ign	ignition
lw	liquid water
m	mixture
ox	oxide
p	particle
u	unburned
V	water vapor zone
v	vaporization
W	liquid water zone
wv	water vapor

heating rates in shock tube experiments [10] are much higher ($\sim 10^6$ K/s) and the oxidizer concentration is different from those employed in other studies. It is also worthwhile to mention that the measured ignition temperature in burner [11,12] and shock tube [10] experiments corresponds to the temperature of the gas. The ignition temperature depends on various parameters such as the particle characteristics, oxidizer concentration, and heating rate. For these reasons, the referenced experimental data cannot be quantitatively compared directly. Nevertheless, it is true that the ignition temperature increases with increasing particle size in the range of 10 nm–100 μm. Even for larger particles, it remains lower than the melting point of the oxide layer, 2350 K. This suggests that the ignition temperatures of aluminum particles in water vapor are lower than those in oxygen. The phenomenon may be attributed to the stabilization of γ-oxide polymorph [8] and/or formation of a weaker hydroxide layer on the particle surface [9].

Many of the desirable traits of nano-sized particles are due to the presence of a large percentage of atoms on the surface [13]. The percentage of atoms on the surface layer of an aluminum

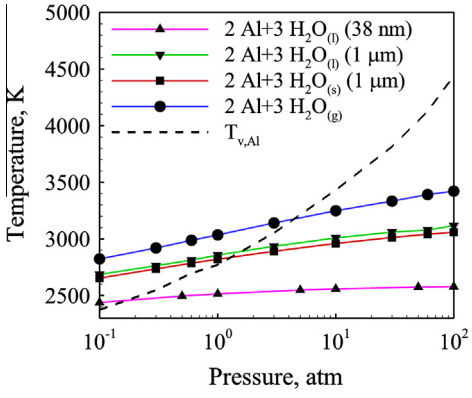

Fig. 1. Effect of pressure on aluminum vaporization temperature and adiabatic flame temperatures for various oxidizers.

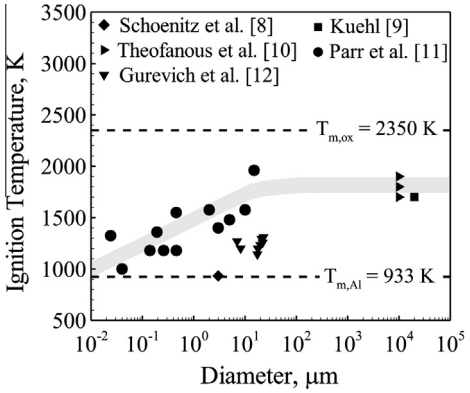

Fig. 2. Effect of particle size on ignition temperature of aluminum particles in water vapor.

particle increases from 2% to 92 %, when the particle size decreases from 100 to 1 nm [13]. The surface atoms have lower coordination numbers and higher energies than the atoms in the interior region of the particle. As a result, the thermophysical properties of nano-sized particles are significantly different from their corresponding bulk values. The melting temperature of nano-aluminum particles decreases from 933 to 473 K when the particle size decreases from 10 to 2 nm [14,15]. Similarly, the melting point of the oxide layer can be lower than the bulk value of 2350 K; for a shell thickness of 2.5 nm the melting point of the oxide layer is 1313 K [16]. The ignition temperatures and burning times of nano-aluminum particles are also lower than their micron-sized counterparts [17]. Significant enhancement in the burning characteristics is, thus, expected, when nano-sized particles are used to formulate energetic materials [18].

The combustion of nano-sized aluminum particles and water has been studied experimentally for a relatively wide range of pressure and particle size [5,19,20]. Results from earlier studies [19,20] suggested that the presence of a gelling agent such as polyacrylamide is necessary to achieve self-sustained deflagration.