A general theory of ignition and combustion of nano- and micron-sized aluminum particles

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ABSTRACT

A general theory of ignition and combustion of nano- and micron-sized aluminum particles is developed. The oxidation process is divided into several stages based on phase transformations and chemical reactions. Characteristic time scales of different processes are compared to identify physicochemical phenomena in each stage. In the first stage, the particle is heated to the melting temperature of the aluminum core. Key processes are heat and mass transfer between the gas and particle surface and diffusion of mass and energy inside the particle. The second stage begins upon melting of the aluminum core. Melting results in pressure buildup, thereby facilitating mass diffusion and/or cracking of the oxide layer. Melting is followed by polymorphic phase transformations, which also results in the formation of openings in the oxide layer. These provide pathways for the molten aluminum to react with the oxidizing gas; the ensuing energy release results in ignition of nano-aluminum particles. For large micron-sized particles, ignition is not achieved due to their greater volumetric heat capacity. In the third stage, nanoparticles undergo vigorous self-sustaining reactions with the oxidizing gas. Reactions typically occur heterogeneously in the particle and the burning rate is controlled by chemical kinetics. For large micron-sized particles, polymorphic phase transformations result in the formation of a crystalline oxide layer. The oxide layer melts and particle ignition is achieved. In the fourth stage, the large micron-sized particle burns through gas-phase or surface reactions, depending on the oxidizer and pressure. The burning rate is controlled by mass diffusion through the gas-phase mixture.

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1. Introduction

Metal particles are attractive fuel candidates for various propulsion and energy-conversion applications. Of all metals, aluminum is popular because of its high energy density, relative safety, and low cost [1]. The enthalpy of combustion of aluminum particles in oxygen at stoichiometric conditions is 84 kJ/cm^3, substantially greater than those of monomolecular energetic materials such as trinitrotoluene (~10–30 kJ/cm^3). Nascent aluminum particles are pyrophoric and react spontaneously in any oxidizing environment [2]. As a result, particles are passivated by exposing them to an oxidizing gas in a well-controlled manner. This results in the formation of an amorphous oxide (Al_2O_3) layer of thickness in the range of 2–4 nm [3,4]. For micron-sized and larger particles, ignition is

commonly associated with melting of the oxide layer at 2350 K [5]. The molten oxide shell forms a cap on the particle surface under the effect of surface tension, thereby exposing the aluminum core to the oxidizing gas. The high ignition temperature and particle agglomeration diminish energy-release rates in various practical applications.

Nanomaterials have unique and favorable physicochemical properties owing to the presence of large percentage of atoms on the surface. The percentage of atoms on the surface layer of an aluminum particle increases from 2% to 92%, when the particle size decreases from 100 to 1 nm. Surface atoms have higher energy than the atoms in interior regions of the particle. As a result, properties are size-dependent and substantially different from those of bulk materials.

Figure 1 shows the effect of particle size on the ignition temperature of aluminum particles [6]. Experimental data are taken from Refs. [5,7–21]. The ignition temperature of aluminum particles decreases with decreasing particle size, from about 2350 K at 100 μm to about 1000 K at 100 nm. Note that there is a considerable scatter in the experimental data owing to differences in experimental conditions including apparatus, sample type, heating

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Nomenclature

a	distance between energy barrier maximum and adjacent minimum
A	surface area
B	transfer number
Bi	Biot number
c	molecular speed
C	concentration
C_p	constant-pressure specific heat
C_v	constant-volume specific heat
D	diameter, diffusivity
E_A	activation energy
h	heat transfer coefficient
h_m	latent heat of melting
h_r	heat of reaction
H_{vap}	heat of vaporization
i	stoichiometric fuel-oxidant mass ratio
K	bulk modulus
k	chemical rate constant
k_B	Boltzmann constant
Kn	Knudsen number
L_v	latent heat of vaporization
m	mass
M	molecular weight
M_p	particle mass
n	number of ions per unit area
N_A	Avogadro's number
p	pressure
Pr	Prandtl number
$\dot{q}$	energy per unit time
Q_r	heat of reaction
R	particle radius, gas constant
Re	Reynolds number
T	temperature
t	time
V	velocity, volume
W	energy barrier
X	mole fraction
Y	mass fraction

Greek letters

β	Knudsen layer thickness
λ	thermal conductivity
τ	time
μ	viscosity
α	energy accommodation coefficient
γ	adiabatic constant
θ	Debye temperature
ρ	density
ε	emissivity
δ	oxide layer thickness
σ	stress, Stefan–Boltzmann constant
Ω	volume per displaced ion
ν	attempt frequency
ϕ	Mott potential

Subscripts

θ	azimuthal
ϕ	polar
a	ambient gas
am	amorphous
b	burn
c	critical, core

cond	conduction
diff	diffusion
frac	fracture
gen	generation
heat	heating
melt	melting
O	oxidizer
ox	oxide
p	particle
poly	polymorphic phase transformation
r	radial
rad	radiation

Superscript

tr	transformation

rate, oxide layer thickness and purity, and oxidizer composition. Care must therefore be taken when comparing data from different experiments. For example, Friedman et al.'s data [5] suggest that ignition temperatures of micron-sized aluminum particles are relatively near the melting point of the oxide film and are not a strong function of particle size. Results of Gurevich et al.'s experiments [15], on the other hand, indicate that ignition temperatures of micron-sized particles are substantially lower than the oxide melting point and decreases significantly with increasing oxidizer concentration. Khaikin et al. [22] proposed that particle ignition in experiments of Friedman et al. [5] is due to particle heating to the melting point of the oxide film, while the trends obtained by Gurevich et al. [15] was explained by considering the crystallization of the oxide layer and thermal inertia of particles. Furthermore, particle impurity (presence of magnesium in the particle) also affects the ignition temperature. As MgO is a non-protective oxide layer, ignition may occur at temperatures lower than the core melting point, as observed by Bulian et al. [10].

Nonetheless, it is apparent that nanoaluminum particles ignite at temperatures as low as ∼1000 K, substantially lower than the bulk melting point of the oxide shell (2350 K). This phenomenon has been attributed to cracking of the oxide layer due melting of the aluminum core [23] and polymorphic phase transformations in the oxide layer [4]. Upon melting, the density of the aluminum core decreases from 2700 to 2400 kg/m^3, an 11.1% change. The molten aluminum core thus exerts tensile stresses and could fracture the oxide layer. The cracks provide pathways for the oxidizing gas to react with the aluminum core. The ensuing energy release results in ignition of nanoaluminum particles. For micron-sized and larger particles, the energy release is insufficient
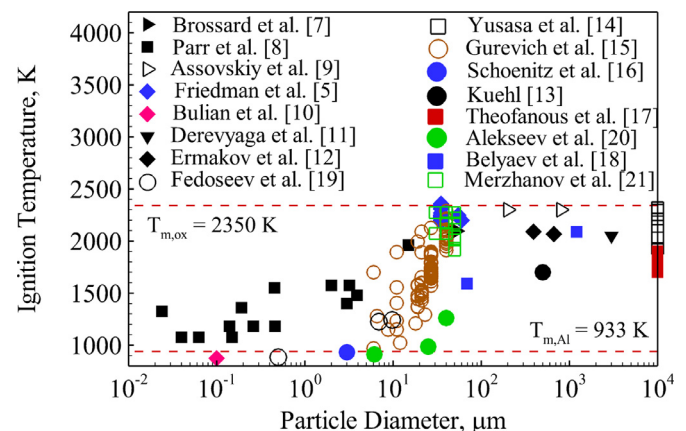

Fig. 1. Effect of particle size on ignition temperature of aluminum particles (adapted from Ref. [6]).