On the role of heterogeneous reactions in aluminum combustion

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ABSTRACT

This work addresses the role of heterogeneous reactions occurring during aluminum combustion. Direct numerical simulations are conducted on a single aluminum burning particle accounting for both detailed gas-phase and surface kinetic mechanism. A surface kinetic solver has been developed to take into account surface and gas/surface interactions. The model is validated against experimental measurements and appears to be predictive. Calculations are performed through different pressure regimes (1 and 10 bar), atmospheres (O_2, CO_2, CO and H_2O) and droplet sizes (from 1 to 400 μm). Flames structures (temperature and AlO profile) computed by the model are consistent with experimental measurements and observations. The reaction zones for CO and H_2O atmospheres are computed to be very close to the surface which is an evidence of a combustion mostly driven by chemical surface phenomena. In some cases surface reactions promote self-sustained combustion for smaller size particles at low pressure regimes. Calculated burning times are also consistent with experimental measurements. In O_2/Ar, surface chemistry is more important when particles are small (under 20 μm) which guides the combustion to a more kinetically-limited regime than a diffusion-limited regime. The importance of surface reactivity is different regarding the particle size and the atmosphere of interest. Calculations of alumina residue size reveals that surface reactions could explain alumina residue formation. The model predicts a strong oxidizer effect on alumina residue size. According to the model, CO_2 environment lead to large residue size while H_2O environment lead to small residue size. This work definitely stresses the potential role of heterogeneous reactions in aluminum combustion.

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1. Introduction

Aluminum particles are widely used for space and military applications to significantly enhance the performances of solid rocket motors. Aluminum reacts with oxidizers released by solid propellant combustion and this leads to an increase in the flame temperature and decrease in the mixture molecular mass. Aluminum is therefore added in solid propellants with mass fraction typically in the range 15∼20%. Large aluminum particles (typically 100 μm or more) mostly burn in vapor phase through a diffusion flame between vaporized aluminum and available oxidizing species (mostly, CO_2 and H_2O in propellant atmospheres) [1]. Combustion of aluminum produces liquid alumina Al_2O_3 that can exist as smokes (size ≈ 1 μm) or larger residues (≈10 μm).

Phenomena accompanying aluminum combustion in propellant gases are very complex and not completely understood so far:

modeling aluminum combustion is still a challenge. The burning time of an aluminum particle is one of the most important parameter. For instance, comparing aluminum burning time with the residence time of aluminum particles in the rocket chamber is helpful to evaluate incomplete combustion loss. This loss arises when slow-burning particles end their combustion outside the rocket chamber. More recently, some studies has pointed out the important role of aluminum burning time on the onset of thermoacoustic instabilities in solid rocket motors [2].

Many modeling efforts have been realized in the last decades focusing on the burning of a single droplet. Direct numerical simulations have been conducted, including multicomponent species diffusion and detailed gas phase chemistry, to address the physics of combustion and the prediction of burning rate in steady [1,3–6] or acoustic unsteady regimes [7]. Present study intends to move a step forward in the physics of aluminum combustion by considering the importance of surface reactivity taking place at the aluminum particle surface. The goal is to investigate to which extent surface chemistry can play a role and eventually gain further insight in aluminum combustion. A more reliable combustion model, accounting for surface chemistry, is expected.

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Nomenclature

A_i	Preexponential factor of reaction i (cm-mol-s-K)
b_i	Temperature exponent of reaction i
$C_{v,\,k}$	Heat capacity at constant volume for the kth species ($J.mol^{-1}.K^{-1}$)
D	Particle diameter (m)
D_{res}	Residue diameter (m)
$\bar{\mathcal{D}}_k$	Mass diffusion coefficient of species k in the mixture ($m^2.s^{-1}$)
E	Total energy ($J.kg^{-1}$)
E_i	Activation energy of reaction i ($J.mol^{-1}$)
h_k	Mass enthalpy of the kth species ($J.kg^{-1}$)
ΔH^o	Enthalpy of reaction ($J.mol^{-1}$)
J_k	Diffusion flux for the kth species ($kg.m^{-2}.s^{-1}$)
k_b	Boltzmann constant ($J.K^{-1}$)
K_g	Total number of gas phase species
K_s	Total number of surface species
$K_{p,\,i}$	Equilibrium constant in pressure units for the ith reaction
$K_{c,\,i}$	Equilibrium constant in concentration units for the ith reaction
$\dot{m}$	Mass rate ($kg.m^{-2}.s^{-1}$)
N_g	Total number of gas phase reactions
N_s	Total number of surface reactions
p	Pressure (Pa)
$\mathbf{q}$	Heat flux ($W.m^{-2}$)
q_i	Rate of progress of the ith reaction ($mol.m^{-3}.s^{-1}$ or $mol.m^{-2}.s^{-1}$)
ΔS^o	Entropy of reaction ($J.mol^{-1}.K^{-1}$)
T	Temperature (K)
T^*	Reduced temperature
t_b	Burning time (s)
u	Velocity in x direction ($m.s^{-1}$)
v	Velocity in y direction ($m.s^{-1}$)
W_k	Molecular mass for the kth species ($kg.mol^{-1}$)
X_k	Molar fraction of the kth species
$[X_k]$	Molar concentration of the kth species (gas or surface) ($mol.m^{-3}$ or $mol.m^{-2}$)
Y_j	Mass fraction of the kth species
γ_i	Sticking coefficient for the ith reaction
Γ	Total density of free sites ($mol.m^{-2}$)
ϵ_k	Minimal Lennard-Jones potential for species k (J)
θ_k	Surface site fraction (or coverage) for the kth species
$\bar{\lambda}$	Mixture thermal conductivity ($W.m^{-1}.K^{-1}$)
$\bar{\mu}$	Gas mixture viscosity for the kth species (Pa.s)
ν_{ki}	Stoichiometric coefficients for species k in elementary reaction i
ρ	Density ($kg.m^{-3}$)
σ_k	Collision diameter for the kth species (m)
ς_k	Number of sites occupied by the kth species
$\Omega^{2,\,2}$	Tabulated collision integral
$\dot{\omega}_k^s$	Mass production rate for the kth surface species ($kg.m^{-2}.s^{-1}$)
$\dot{\omega}_k^g$	Mass production rate for the kth species due to gas-phase reactions ($kg.m^{-3}.s^{-1}$)

Indeed, past experimental works have pointed out a potential important role of heterogeneous reactions at aluminum surface during combustion. They have shown that two major parameters greatly influence the role and importance of surface chemistry during burning: particle size and the nature of surrounding atmosphere. Experimental efforts conducted by Bazyn et al. [8] and Lynch et al. [9] report evidence of a transition of diffusion to kinetic controlled combustion. For small size burning droplets, diffusion becomes faster relative to reaction rates and the flame moves closer to surface. At this point, droplet surface and near-surface can have high oxidizer concentration and surface reactivity is expected to be promoted. The atmosphere composition can also highly influence surface reactivity. Sarou-Kanian et al. [10] observed aluminum carbide (Al_4C_3) island appearing on the droplet surface for highly concentrated carbon dioxide atmospheres. AlO emission measurements from Glumac et al. [11] show the existence of a surface or near-surface reacting zone for small particles (5 to 10 μm) burning in CO_2 diluted environments. Bucher et al. [12] reports the possibility of oxidation by heterogeneous reactions at the surface of particles that burn in a pure CO atmosphere. The authors observed that the combustion occurs without any gas-phase flame envelope around the droplet, suggesting a major role of surface reactions. Concerning aluminum burning in water vapor, Gill et al. [13] mentioned an optical signature of the burning particle weaker than in other environments, which probably indicates a primarily surface oxidation. Surface processes are also pointed out by Dufaud et al. [14]. They assume that water chemisorbs at aluminum surface and then generates H_2 in the gas phase, which can enhance explosion severity of aluminum dust in water environments. Nitrogen containing environments can also induce surface reactivity. Sarou-Kanian et al. [15] and Gromov et al. [16] observed aluminum nitride (AlN) formation at the surface droplets burning in N_2 containing atmospheres.

As mentioned previously, the burning time τ_b of a particle is a major controlling parameter for aluminized propellant rockets. It is widely described as a power-law $\tau_b = aD^n$ with a and n are parameters determined empirically, and D the initial particle diameter. Beckstead [1,17,18] determined some correlations to calculate burning times depending on particle diameter, pressure and oxidizer concentrations in the gas phase. For aluminum particles, the size dependence of the burning time usually does not follow the classical D^2-law – expected for diffusion flames – but a more general D^n model, with n ranging from 1.5 to 2.0. It is found that there is a weak dependence on ambient pressure and temperature but a significant effect of oxidizer concentrations with aluminum burning faster in O_2 than in H_2O or CO_2. Later on, Lynch et al. [9] showed that these correlations were no longer valid for particles smaller than 20 μm and stated that in this case n was smaller than 1.5. Exponent n is even smaller ($n \approx 0.3$) for nanometric particles [19].

Another important aspect related to aluminum combustion is the formation of liquid alumina $Al_2O_{3,\,(l)}$ which is the main combustion product. It is predominantly present as fine particles, or smokes, with size $D_{smoke} \approx 1$ μm, but can also be produced as larger residues ($D_{res} \approx 10$ μm or more) that might come from the alumina cap that grows on the aluminum particle during combustion. The knowledge concerning those large alumina residues is currently limited and their exact origin and physics of formation is poorly known. The size D_{res} of alumina residues is also crucial in the frame of solid propulsion since it primarily controls the extent of two-phase losses in the nozzle. Salita [20] compiled experimental results from different sources and deduced a simple law to predict residues diameter. Alumina residue diameter D_{res} is more easily expressed as the ratio β between the residue size and initial particle size D_0 : $\beta = D_{res}/D_0$. Turns et al. [21] experimentally deduced a β between 0.6 and 0.8. In a similar experimental study by Glotov and Zhukov [22], β was in the range 0.5~0.8 for different diameters and oxidizers. Simulations from Marion et al. [23] based on a Law's model agree with this range of 0.6 to 0.8. However recent experimental studies using a quench bomb [24] report a β significantly lower, about 0.1~0.2, which depends on the oxidizer nature. Therefore there are large discrepancies for that parameter which urges an improved understanding for the formation of large residues. Due to the possibility of surface chemistry, alumina cap