

## Models for Fast Combustion Waves in Nanocomposite Thermite Powders

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### ABSTRACT

The combustion of nanometric aluminum (Al) powder with an oxidizer such as molybdenum trioxide (MoO<sub>3</sub>) is studied analytically. The analysis was performed to identify combustion wave propagation models that are in concurrence with experimental results from flame tube experiments. Both deflagration and detonation models were investigated. In the deflagration models, individual Al particle gasification characteristics were evaluated to determine whether powder deflagrations would propagate in a fashion such that particles would evaporate before entering the primary reaction zone. Evaluation of characteristic times relevant to propagation of a deflagration reveals that particles only less than about 1.7 nm in diameter evaporate before appreciable chemical reactions occur. Because experimental studies typically use Al particles greater than 1.7 nm in diameter, it is concluded that nanocomposite powder deflagrations would typically be controlled by multiphase diffusion effects and particle interactions. Deflagration models based on particle interactions and multiphase diffusion, however, predict orders of magnitude slower propagation rates than what are experimentally observed. This study also considers detonation wave models and uses a one-dimensional Chapman-Jouget approach. Detonation waves are analyzed assuming both frozen and equilibrium sound speeds in multiphase mixtures. Wave speeds that are in basic agreement with experimental data are obtained provided that multiphase equilibrium sound speeds are applied at the downstream edge of the detonation wave. The results indicate that the fast combustion waves observed with nanocomposite Al-MoO<sub>3</sub> powder mixtures are likely multiphase detonations and that equilibrium sound speeds of multiphase mixtures play an important role in determining speeds of fast combustion waves.

### INTRODUCTION

Nanoparticle aluminum oxidation has shown accelerated reactivity beyond what classical diffusion theories predict [1]. A consequence of this reactivity is the fact that combustion wave speeds in nanocomposite powder mixtures can be very fast, e.g., 1000 m/s [1,2]. Partly from flame propagation observations made in flame tube experiments, many have tried to explain the fast reaction propagation associated with nano-Al particles using advanced diffusion-based reaction mechanisms [2-10]. However, these studies have not been successful in providing models that compare well with experimental data, e.g., for combustion wave speeds and downstream pressures. In this study we investigate deflagration and detonation models to identify combustion wave propagation models that are in concurrence with experimental results for rapid flame propagation rates observed in flame tube experiments.

The deflagration of a nanocomposite powder will be considered first. This study will examine the characteristic times associated with particle gasification and the results will then be used in a simplified deflagration model. Following this, the Chapman-Jouget detonation modeling studies will be presented.

## DEFLAGRATION MODELING

This model considers that the reactants, i.e., nanometric Al and MoO<sub>3</sub>, first enter a preheat zone where they are heated by diffusion of heat from the upstream reaction zone. As the MoO<sub>3</sub> particles heat, it is assumed that they rapidly produce gaseous oxygen, which is taken to be O<sub>2</sub>. The Al particles will also heat up in the preheat zone. If the Al particles are sufficiently small, they will completely gasify before entering the reaction zone. It is also possible for Al particles to partially gasify and then enter the reaction zone, where they complete their gasification histories over timescales that are commensurate with preheat and chemical kinetic timescales. Because flame propagation characteristics may be appreciably different depending on which scenario is most closely approached, we first examine characteristic times for aluminum droplet evaporation, where it is noted that we are assuming that molten aluminum droplets are present, i.e., we neglect solid-liquid phase changes.

In this analysis, where we relate macroscopic flame propagation experiments to the behavior of a single particle, we consider two characteristic times as follows.

$\tau_{\text{tube}}$ : Characteristic particle residence time in the flame zone in a flame that propagates through the powder media.

$\tau_{\text{evap}}$ : Characteristic molten Al droplet evaporation time.

### *Particle Residence Times in the Flame Zone*

This parameter is based on flame speeds measured in a flame tube. In this study  $\tau_{\text{tube}}$  will be evaluated for a representative Al+MoO<sub>3</sub> reaction that has a 960 m/s flame speed [2]. As a conservative estimate, the flame zone thickness will be assumed to be the thickness of the preheat region, i.e.,  $\tau_{\text{tube}} = \alpha/S_L^2$  where  $\alpha$  is thermal diffusivity and  $S_L$  is the flame speed.

The thermal diffusivity is calculated as  $\alpha = 2.46 \times 10^{-5} \text{ m}^2/\text{s}$  and the flame speed used in this analysis is 960 m/s as measured from experiments [2]. We thus calculate particle residence times in the flame zone as  $\tau_{\text{tube}} = 2.67 \times 10^{-11} \text{ s}$ .

### *Molten Al Droplet Evaporation Times*

Because we are considering nanometric Al particles, we need to assess the effects of the particle mean-free-path on gasification behaviors. At 1600 K and 1.5 MPa, estimates indicate that a characteristic gas-phase mean-free-path,  $\lambda$ , is roughly 25 nm. As such, it is possible for nanometric Al particles to be larger or smaller than  $\lambda$ , and we thus consider droplet evaporation models for the continuum limit as well as the free molecular flow limit.

### *Continuum Limit Droplet Evaporation Model*

This model utilizes classical expressions for evaporation of a droplet [11]. A characteristic time for evaporation in the continuum limit is defined in Eq. (1) where other relevant variables are evaluated using Eqs. (2) and (3).

$$\tau_{\text{evap,cont}} = \frac{d_0^2}{K} \quad (1)$$

$$K = \frac{8k_g}{\rho_l c_{pg}} \ln(B_T + 1) \quad (2)$$

$$k_g = 0.4k_f(\bar{T}) + 0.6k_\infty(\bar{T}) \quad (3)$$

$$B_T \equiv \frac{c_p(T_\infty - T_s)}{h_{fg}} \quad (4)$$

In the above equations:  $d_o$  is the condensed phase initial droplet diameter,  $k_f$  and  $k_\infty$  are the thermal conductivities of the fuel vapor and surroundings, respectively,  $\rho_l$  is the liquid density,  $c_{pg}$  is the constant-pressure specific heat of the gas mixture (weighted average of fuel vapor and surroundings),  $T_f$  is the flame temperature for the reaction (3022 K),  $c_p$  corresponds to Al at the flame temperature (1176 J/kgK) and  $h_{fg}$  is the enthalpy of vaporization at the flame temperature ( $3.19 \times 10^6$  J/kg). For this model, the droplet temperature must be known and this temperature depends on pressure. For calculation of  $\tau_{evap,cont}$ , evaporation in quiescent hot air is assumed. The transfer number  $B_T$  is calculated to 0.13, the evaporation rate constant is  $K = 1.0673 \times 10^{-7}$  m<sup>2</sup>/s and the characteristic droplet evaporation time is a function of the droplet diameter and is evaluated to be  $\tau_{evap,cont} = 9.37 \times 10^6 d_o^2$  where  $d_o$  is the initial droplet diameter in m and the evaporation time is in seconds.

#### Free Molecular Limit Droplet Evaporation Model

In the free molecular limit, the particles are assumed to be significantly smaller than the local gas-phase mean free path. We will consider evaporation of a droplet in this limit under the assumption that droplet heating is negligible, i.e., that the droplet temperature is quasisteady. Analyses show that the droplet lifetime in the free-molecular limit,  $\tau_{evap,fm}$ , is given by Eq. (5)

$$\tau_{evap,fm} = d_o / \phi \quad (5)$$

where  $\phi$  is a parameter that depends on factors such as the partial pressure of Al and the rates that Al atoms enter and leave a droplet. Calculations yield the result that  $\tau_{evap,fm} = 23/d_o$  for the conditions of interest here where  $d_o$  is the initial droplet diameter in m and the evaporation time is in seconds.

Comparison of these evaporation times shows that for the nanoparticles of interest here, droplets are predicted to evaporate more slowly in the free-molecular limit than the continuum limit, i.e., as droplets become small the continuum-limit model will over-predict droplet evaporation rates.

The characteristic times are plotted in Fig. 1. The curves show that  $\tau_{tube}$  is equal to  $\tau_{evap,cont}$  and  $\tau_{evap,fm}$  at diameters of about 1.68 and 0.0012 nm, respectively. These diameters are appreciably less than or roughly equal to the gas-phase mean free path, taken to be 25 nm, such that free molecular limit theory should apply for predicting droplet diameters below which purely gas phase reactions will dominate. However, the  $d_o$  value for the free-molecular theory (where  $\tau_{tube} = \tau_{evap,fm}$ ) is so small that all particles are predicted to burn in a multiphase fashion rather than with a gas phase reaction zone preceded by a droplet evaporation zone.

Because multiphase combustion is predicted, we will employ a diffusion-based interacting particle model to calculate deflagration speeds and also to evaluate whether deflagration models are appropriate. For this purpose a correlation for solid fuel burning is used from Williams [12]. In that study, Williams examines the flame spread in black powder using random walk theory and shows that by combustion alone the spread rate is about two orders of magnitude less than the individual particle surface regression rate. Specifically, 60 cm/s compared to 5000 cm/s for black powder. Along these lines, the spread rate for Al droplets of about 100 nm in diameter may be on the order of 0.003 m/s, where we have employed an average droplet surface regression rate. Because this flame spread rate is orders-

of-magnitude smaller than what is observed in flame tube experiments, we will now consider detonation models in an attempt to obtain better agreement with experiments. It is also noted that for nanometric scale particles, Reynolds numbers associated with flame speeds of 1000 m/s are on the order of unity. If particles agglomerate, though, Re will increase and convective influences may become more dominant.

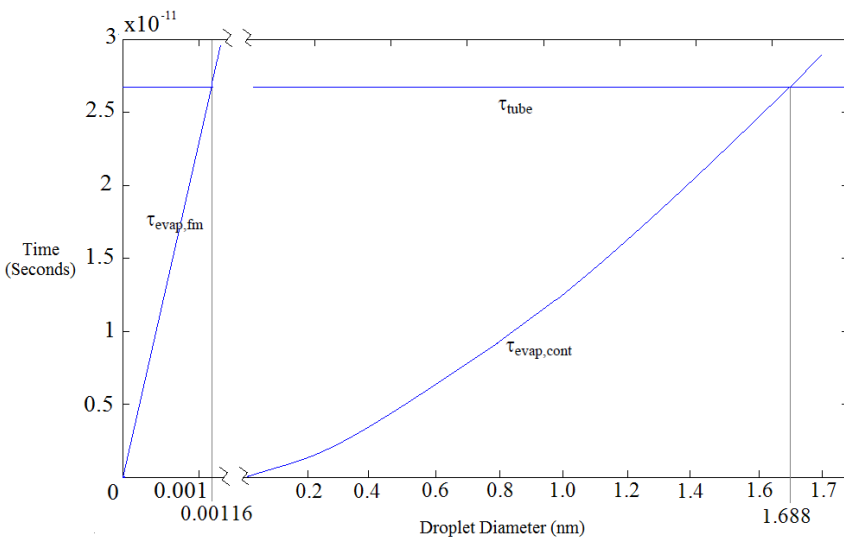


Figure 1. Characteristic times as a function of droplet diameter. For all diameters illustrated in this figure the free molecular limit is most applicable (i.e.,  $d_0 \leq 25$  nm).

## DETONATION MODELING

For this analysis, we do not consider details of the detonation wave structure but instead perform a one-dimensional planar analysis that considers only the initial (reactant) and final (product) states. We also assume that Chapman-Jouget detonations are prevalent. For a Chapman-Jouget detonation, the downstream velocity,  $v_2$ , is equal to the speed of sound of the products,  $a_2$ , in a reference frame that is stationary with respect to the combustion wave.

As discussed by Rudinger [13-14] there are two limiting sound speeds that apply to particle-laden gases, i.e., the frozen sound speed, denoted by  $a_f$ , and the equilibrium sound speed, denoted by  $a_e$ . The frozen sound speed applies when the solid particles change their state infinitely slowly such that they cannot follow changes in the gas. In contrast, the equilibrium sound speed applies when the particles and the gas are in equilibrium with each other at all times. The equilibrium sound speed would be most closely approached for small particles, which equilibrate rapidly, or when sufficient time is available for equilibration.

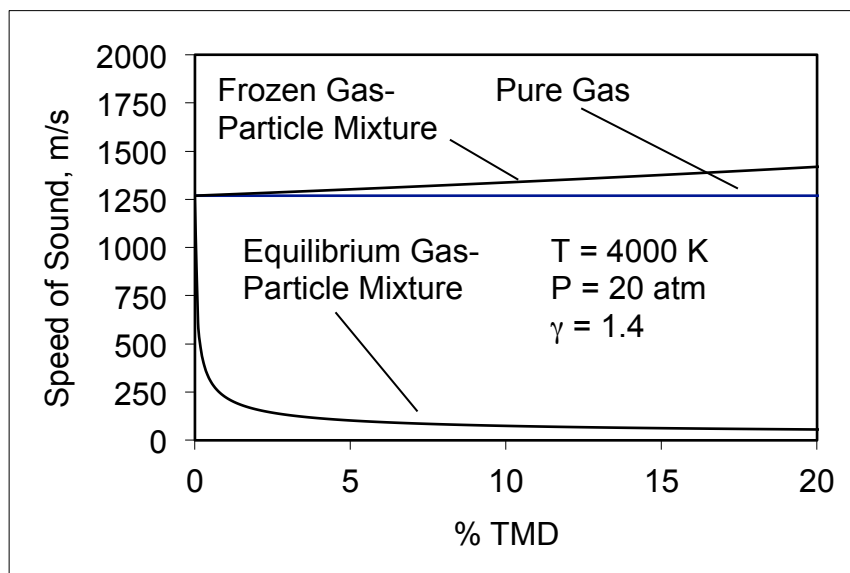


Figure 2. Representative sound speeds as a function of % TMD.

Even for modest values of % TMD, equilibrium sound speeds can be of the order of 100 m/s or less. This is important for detonation calculations when mass conservation across the detonation wave is considered, i.e., Eq. (6).

$$\rho_1 v_1 = \rho_2 v_2 \quad (6)$$

The variable  $v_1$  is the combustion wavespeed and  $\rho_1$  is the static density of the upstream reactants. By solving Eq. (6) for  $v_1$  and imposing the Chapman-Jouget condition,  $v_2 = a_2$ , we obtain the following relation for the detonation wave speed  $v_1$ .

$$v_1 = (\rho_2 / \rho_1) a_2 \quad (7)$$

Equation (7) shows that if  $a_2$  decreases strongly, then so does the wave speed  $v_1$ , where calculations indicate for detonations of the types considered here, the ratio  $\rho_2/\rho_1$  varies by about a factor of two or less such that variations in  $v_1$  are most strongly influenced by variations in  $a_2$ . These calculations consider energy, momentum and mass conservation. It is also noted that the calculations predict product pressures that are similar to experimentally measured values.

Experiments on combustion of nanoscale Al-MoO<sub>3</sub> powders have demonstrated [15] that for small % TMD values, the combustion wave propagation velocity decreases significantly as the % TMD of the reactants increases. Considering Eq. (7) and Fig. (2), this indicates that detonations in nanoscale Al-MoO<sub>3</sub> powders may be strongly influenced by the equilibrium sound speed of the products, which will in general contain gas-phase species as well as condensed-phase species. Though not shown here because of manuscript size limits, analytical and computer modeling of multiphase detonations verify these predictions.

## CONCLUSIONS

The combustion of nanometric aluminum (Al) powder with an oxidizer such as molybdenum trioxide (MoO<sub>3</sub>) was studied analytically. We considered both deflagration and detonation models. The models suggest that deflagration speeds are much slower than the fast wave speeds observed in experiments. A Chapman-Jouget detonation model, however, provides reasonable agreement with experimental wave speeds provided that multiphase equilibrium sound speeds are applied at the downstream edge of the detonation wave. The

results indicate that equilibrium sound speeds of multiphase mixtures can play a critical role in determining speeds of fast combustion waves in nanoscale Al-MoO<sub>3</sub> powder mixtures. It is expected that these results may also apply to other nanoscale mixtures that exhibit fast combustion waves.

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