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Computational Modeling of Combustion Wave in Nanoscale Thermite Reaction

Kyoungjin Kim

***Abstract*—**Nanoscale thermites such as the composite mixture of nano-sized aluminum and molybdenum trioxide powders possess several technical advantages such as much higher reaction rate and shorter ignition delay, when compared to the conventional energetic formulations made of micron-sized metal and oxidizer particles. In this study, the self-propagation of combustion wave in compacted pellets of nanoscale thermite composites is modeled and computationally investigated by utilizing the activation energy reduction of aluminum particles due to nanoscale particle sizes. The present computational model predicts the speed of combustion wave propagation which is good agreement with the corresponding experiments of thermite reaction. Also, several characteristics of thermite reaction in nanoscale composites are discussed including the ignition delay and combustion wave structures.

***Keywords*—**Nanoparticles, Thermite reaction, Combustion wave, Numerical modeling.

I. Introduction

IN the technical field of nanoenergetics, the use of highly reactive metallic powders produced in nanoscale particle sizes can dramatically increase the energetic performances in various military or civilian applications such as explosives, propellants, and pyrotechnic devices [1]. When compared to the conventional micron-sized metallic powders, nanoscale powders such as aluminum nanoparticles show much faster heat releasing reaction and more complete combustion along with much shorter ignition delay [2]-[4].

When the aluminum nanopowder is mixed with nanoscale metal oxidizer such as molybdenum trioxide (MoO_3), it becomes a highly reactive thermite formulation. This nanoscale thermite reaction exhibits quite a rapid, highly exothermic combustion with high-energy release:

$$2Al + MoO_3 \rightarrow Al_2O_3 + Mo + 4.7\ kJ/g$$

A nanoscale thermite mixture can provide an ability to release energy in a controllable fashion along with high energy density. Also, since the reaction gives benign by-products, the nanoscale thermite can be a viable candidate as replacement for conventional lead-based ammunition primers and pyrotechnic formulations [5], [6].

In recent years, there have been many investigations on the combustion characteristics of nanoscale thermite formulation [7]-[9]. Among them, Granier and Pantoya [10] studied the flame propagation in consolidated pellets made of the nanoscale Al/MoO_3 thermite composites using nanosized aluminum powders of an average particle size ranging from 20 to 200 nm mixed with nanoscale MoO_3 flakes of approximately 20 nm thickness. Nanoscale composite thermite pellets of cylindrical shape were produced by compacting nanoscale thermite powders with die compression loads and the thermite pellet samples were ignited using laser power. Their experimental measurements showed that the nanoscale thermite pellets have exceptionally high burn rates on the order of 10 m/s. The ignition delay time was reduced by an order of magnitude compared to the conventional energetic materials with micron-sized Al/MoO_3 particles.

In this research, a simplified modeling analysis based upon self-propagating combustion waves has been established to predict and appreciate the ignition and combustion propagation characteristics in the consolidated Al/MoO_3 nanoscale thermite composite pellets.

Kyoungjin Kim is with the Department of Mechanical System Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 730-701, Republic of Korea (phone: 82-54-478-7327; fax: 82-54-478-7319; e-mail: kimkj@kumoh.ac.kr).

II. Computational Modeling

In the present study on the analytic modeling of thermite reaction in Al/MoO_3 nanoscale composite pellet, it is assumed that the reaction front propagates in a manner similar to that of homogeneous combustion waves, despite the heterogeneous nature of particle mixture. In this way, we assume that width of the reaction zone is much larger than the reactant particle size. Thus, the combustion wave propagation is not affected by the heterogeneous microstructure of the medium and thus moves uniformly.

Figs. 1 and 2 illustrate the typical reaction characteristics of a self-propagating combustion wave in reactant-oxidizer system. The reactant fraction (η) or completion degree of reaction rapidly changes from one to zero across the reaction zone where the heat releasing reaction takes place. The temperature changes more slowly from combustion temperature (T_c) to the initial temperature (T_0) of the unreacted medium. Heat diffusion occurs ahead of the combustion wave by creating the preheating zone. The energy equation for the one-dimensional thermite reaction and heat diffusion model [11] can be expressed as

$$\frac{\partial(\rho cT)}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) + \rho H_f \Phi \quad (1)$$

where t is the time, T is the temperature, ρ is the mass density, c is the specific heat, k is the thermal conductivity of the consolidated composite pellet, while H_f is the exothermic heat of the chemical reaction. By assuming the Arrhenius chemical

kinetics, the reaction rate Φ is given as

$$\Phi = \frac{\partial \eta}{\partial t} = A_0 (1-\eta) \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where E_a is the activation energy, R is the universal gas constant, and A_0 is the pre-exponential factor. The composite density is expressed as $\rho = (1-\varphi)\rho_0$ for the consolidated thermite pellet, where ρ_0 is the composite density when the porosity φ is zero. The effective thermal conductivity is estimated by the following relation

$$k = k_1 \frac{1 + 2k_1/k_2 - 2\psi(k_1/k_2 - 1)}{1 + 2k_1/k_2 + \psi(k_1/k_2 - 1)} \quad (3)$$

where k_1 and k_2 are the thermal conductivities of MoO_3 and aluminum, respectively, and ψ is the volume ratio of aluminum to MoO_3. In this study, the porosity of the pellet is 60 percent, and this value corresponds to the experiments [10].

Due to the thickness of reaction zone, determination of the speed for the combustion wave propagation can be somewhat arbitrary. Therefore, in this study, it is estimated by evaluating the time derivative for spatial integration of reactant fraction such as

$$V_{CW} = \frac{dx_{CW}}{dt} = \frac{d}{dt}\int_0^x \eta \, dx \quad (4)$$

Ignition of consolidated nanoscale thermite by laser power in the experiments is effectively simulated by imposing varying degree of surface heat flux at the left side of the computational domain (x=0), until the self-propagation of thermite reaction front is well established. The right side of domain is thermally insulated, assuming the domain length is large enough.

A series of transient one-dimensional computations were performed by solving (1) and (2) simultaneously using COMSOL Multiphysics software (version 4.3). The present study employed the computational domain of 0.9 mm and more than 5,000 grid points are used to resolve the rapid changes of properties due to the very thin reaction zone.

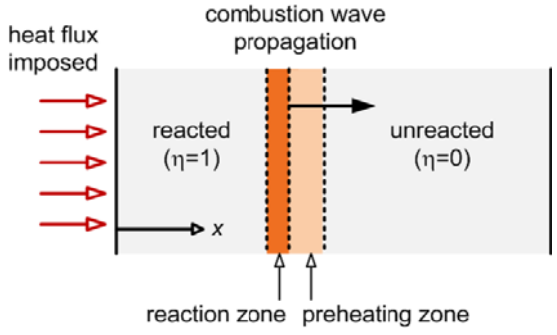


Fig. 1 Combustion wave propagation in nanoscale thermite reaction

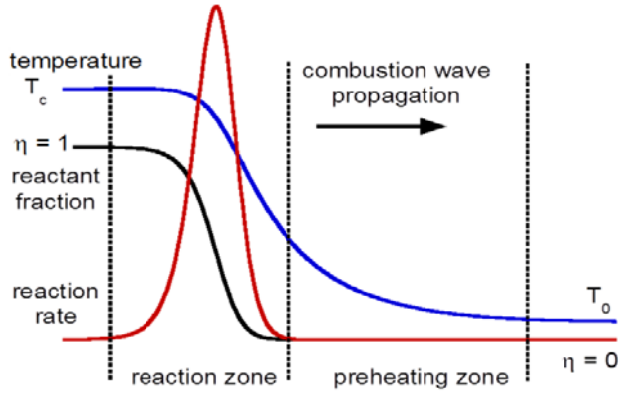


Fig. 2 Preheating and reaction zones in nanoscale thermite reaction

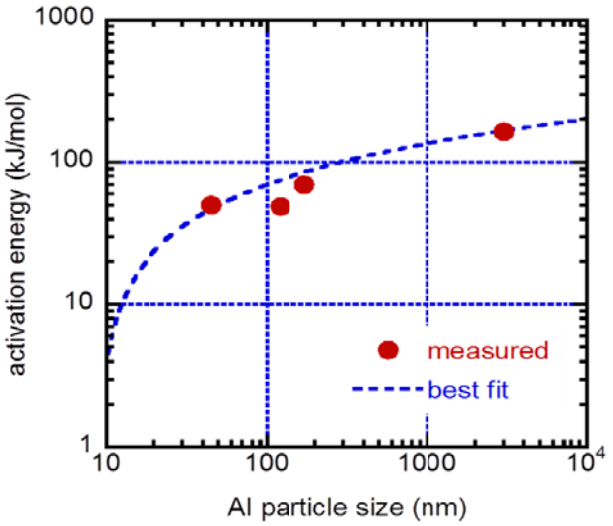


Fig. 3 Change of activation energy of nanosized aluminum powder by particle size (measurements by Aumann et al. [12])

III. Results and Discussion

The ignition and reaction of energetic materials heavily depends on the particle size, and, generally, using smaller particles in the material may enhance the reactivity and flame propagation speed, due to the increased diffusion and heat conduction. Since the diffusion length scale is much smaller and the fuel/oxidizer composition is much more homogeneous in nanoscale composite materials compared to the micron-sized thermites, the combustion wave propagation in nanoscale thermites will be much faster with shorter ignition time.

As Aumann et al. [12] studied the oxidation behavior of nanoscale aluminum powders; it is found that nanoscale aluminum powders showed lower activation energy than larger sized particles. They examined the aluminum nanoparticles with the specific surface areas of 49, 19, and 13 m^2/g, which corresponded to the BET-based average particle diameter of 45, 120, and 172 nm, and measured the activation energy of 50, 49, and 70 kJ/mol, respectively. For the micron-sized aluminum particles, the activation energy was 170 kJ/mol.

Thus, this work will incorporate the nanoscale particle effects by relating the activation energy to reactant particle size

of aluminum, as shown in Fig. 3. Note that the conventional modeling on the self-propagating combustion of micron-sized powders usually modifies the pre-exponential factor to include the particle size effects.

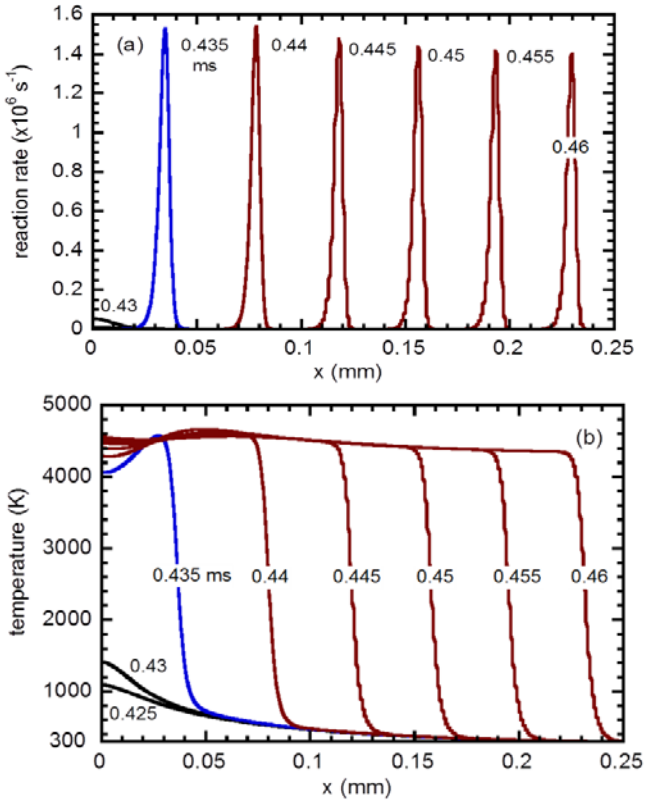


Fig. 4 Temporal changes of reaction rate (a) and temperature (b) in nanoscale thermite reaction (E_a = 70 kJ/mol, q_{im} = 200 MW/m^2)

In addition, although the measurements of activation energy were from the oxidation of aluminum powders with oxygen gas [12], we have used this data for the thermite reaction, since it is reasonably assumed that the decomposition of oxygen from the nano-sized oxidizer of MoO_3 sublimation occurs on a time scale comparable to the experiments.

Fig. 4 shows the temporal changes of reaction rate (Φ) and temperature in nanoscale thermite around the time of reaction initiation for the case where the aluminum activation energy is 70 kJ/mol (or the corresponding particle size of 100 nm), while the imposed heat flux is 200 MW/m^2. From the initial time of heat flux imposing (t=0), heat diffuses into the pellet and it takes some delay to start the thermite reaction when the time is approximately 0.43 ms. After the initiation of thermite reaction, the combustion wave front propagates steadily and its speed becomes constant at approximately 7.1 m/s. This predicted combustion wave speed is quite comparable with the measured value of 6.6 m/s [10]. Also, judging from the reaction rate in each time after the self-propagation of thermite reaction is the established, the reaction zone is estimated to be approximately 10 μm in width.

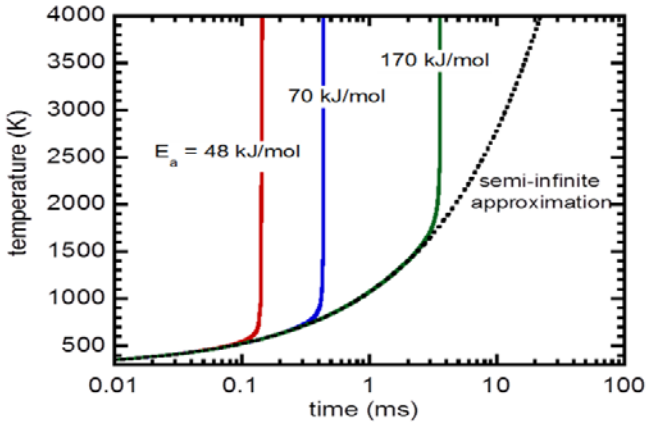


Fig. 5 Effects of activation energy on temporal changes of boundary temperature in nanoscale thermite reaction (q_{im} = 200 MW/m^2)

At this time, three different activation energy levels of 48, 70, 170 kJ/mol, which corresponds to the aluminum particle size of roughly 40, 100 nm, and 2-3 μm with the identical heat flux imposed (200 MW/m^2), are tested in order to appreciate the effects of particle size reduction in thermite composite. Fig. 5 shows the change of temperature at the wall where the heat flux is imposed. In the figure, the dotted line represents the wall temperature change without heat release from the reaction by assuming the heat diffusion into the semi-infinite solid and it is expressed as the relation of [13]

$$T(x=0,t)-T_0=\frac{2q_{im}}{k}\left(\frac{\alpha t}{\pi}\right)^{1/2} \quad (5)$$

where α represents the thermal diffusivity of thermite pellet. Therefore, the departure of temperature from this semi-infinite solid approximation and subsequent temperature increase in a drastic manner exhibits the initiation of thermite reaction for each case of different level of activation energy or particle size. The ignition times for E_a = 48, 70, 170 kJ/mol are found to be 0.14, 0.43, and 3.6 ms, respectively, showing that the ignition delay for micron-sized thermite is an order of magnitude larger than the ones for nanoscale thermite composites. Also, note that the ignition takes place at much lower temperature at nanoscale composites than the micron-sized pellets, and the nanoscale requires much less preheating before initiating the thermite reaction.

The effects of reduction in activation energy by use of nanoparticles in thermite composites on the ignition delay and the speed of self-propagating combustion wave are summarized in Fig. 6. The increase of imposed heat flux results in faster ignition of the thermite pellet. In each case of activation energy, the ignition delay decreases to approximately one-tenth when the imposed heat flux increases from 100 to 400 MW/m^2, as shown in Fig. 6 (a). In general, nanoscale thermites demonstrate the much faster ignition than the micron-sized ones, which may benefit the designing the initiation devices of propellants or explosives. The precise control of ignition delay in nanoscale thermite might be possible by adjusting the imposed heat flux (or laser power in the experiments).

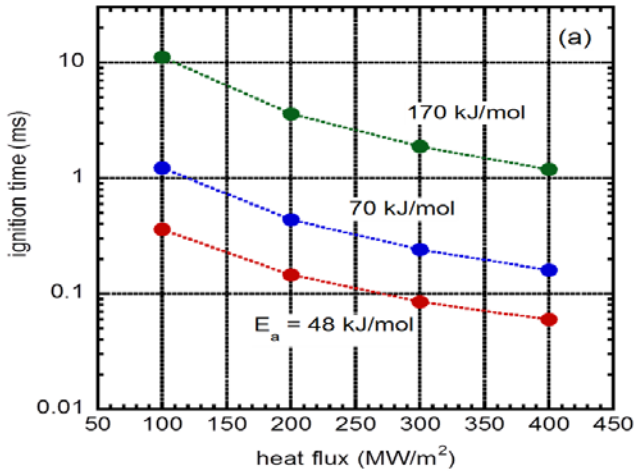
Alternatively, the ignition delay could be changed by controlling the mixture ratio of reactant and oxidizer in thermite composites.

In the experiments of nanoscale thermite ignition [10], the burn rate or combustion wave speed was measured for composite pellets made from thermite mixture with different particle sizes. Those experimental results are compared with the prediction of combustion wave speed from the present analytical modeling in this study. The agreement is quite favorable, as can be seen in Fig. 6 (b).

For the case of activation energy of 48 kJ/mol (or aluminum particle size of 40 nm), the prediction shows the combustion wave speed of 11.7 m/s, while the measured speed is 11.2 m/s. For the activation energy of 48 kJ/mol (particle size of approximately 100 nm), predicted and measured speeds are 7.1 and 6.6 m/s, respectively. In contrast, the micron-sized thermite samples (E_a = 170 kJ/mol for 2-3 μm aluminum particles in thermite composites), the combustion wave speed is found to be much slower at 1.1 (predicted) or 1.2 m/s (measured).

IV. Conclusions

As the nanoenergetics materials such as nanoscale thermites exhibit several technical advantages over the conventional micron-sized energetic formulations, this paper introduces the one-dimensional time-dependent computational model for the prediction of combustion wave propagation in compacted pellets made of nanoscale Al/MoO_3 thermite with the inclusion of activation energy reduction in the oxidation of nano-sized aluminum powders. The reaction ignition of thermite pellets is simulated by imposing the heat flux and the computational results shows the self-propagation of thermite reaction front. When compared to the experimental results, the agreement of combustion wave speed depending on the level of activation energy or reactant particle size is found to be quite favorable.



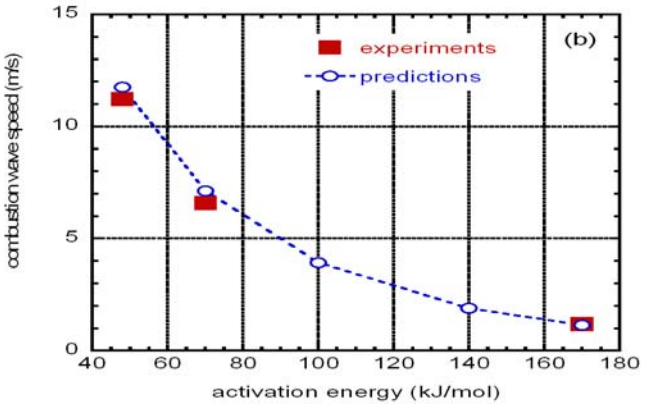


Fig. 6 Effects of activation energy on ignition time and combustion wave speed in nanoscale thermite reaction

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Kyoungjin Kim received the B.S. and M.S. degrees from Seoul National University in 1988 and 1990, respectively, and the Ph.D. degree from The University of Texas at Austin in 1998, all in the academic area of mechanical engineering. He is presently the faculty member of Department of Mechanical System Engineering at Kumoh National Institute of Technology in Gumi, Korea. His research interests include the numerical modeling of fluid flow and heat transfer phenomena in materials processing and microflows, CFD on the plasma arc discharge, and R&D in the optical fiber manufacturing and the semiconductor wafer processing technologies.