# Self-Heating Model of Spherical Aluminum Nanoparticle Oxidation

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**Abstract**

Aluminum-oxygen reaction is important in highly energetic and high pressure generating systems. Nanoenergetic thermites include mixtures of nanostructured Al and oxidizer particles. The main distinguishing features of these reactive systems are their significant enthalpy release and tunable rate of energy discharge, which gives rise to a wide range of combustion rates, energy release, and ignition sensitivity. In this paper, we consider rapid oxidation of a spherically symmetric aluminum particle. We use the Cabrera Mott oxidation model to describe the kinetics of oxide growth of an aluminum nanoparticle and to predict reaction temperature and oxidation time. We assume that aluminum particle of diameter 10 to 50 nm is covered by a thin oxide layer (1-4 nm) and is surrounded by abundant amount of oxygen stored by oxidizers. The particle is rapidly heated up to ignition temperature to initiate self-sustaining oxidation reaction as a result of highly exothermic reaction. We numerically investigated the oxidation model by using COMSOL multiphysics software. The software creates a mesh fitted to geometric configuration of a nanoparticle, and performs finite element method computations.

*Keywords:* Nanoenergetic thermites, Aluminum oxidation, Cabrera-Mott model, Self-heating.

## Introduction

Several studies have been directed to understand the mechanism and kinetics of aluminum particle oxidation [1-4]. Aluminum oxidation exhibits high enthalpy release and has been extensively used for propulsion, pyrotechnics and explosion reactions [5]. Nanoenergetic materials (NM) based on aluminum thermites may store two times more energy per volume than conventional monomolecular energetic materials [3, 6]. The size reduction of reactant powders such as aluminum from micro- to nano-size increases the reaction velocity in some systems by two to three orders of magnitude [8-9]. Among numerous thermodynamically feasible nanostructured energetic mixtures the most widely investigated are $Al/Fe_2O_3$, $Al/MoO_3$, $Al/WO_3$, $Al/CuO$, $Al/Bi_2O_3$ and $Al/I_2O_5$ nano systems [8-16].

Our recent experiments suggest that oxidation of nanoparticles of aluminum with $Bi_2O_3$ and $I_2O_5$ occurs in a few microseconds or less [13-15]. Rapid reaction in the nanostructured thermites cannot be explained by a conventional mechanism based on the diffusion of Al and O atoms in oxides.

In this report, we present a rapid oxidation model of spherical aluminum nanoparticles surrounded by oxygen, using the Cabrera-Mott oxidation model [3-4, 7] with a self- consistent potential. The effects of self-heating are very significant in such model, as we are dealing with a highly exothermic reaction, and since the oxidation rates are very sensitive to the reaction temperature. To estimate the temperature of the nanostructured particle throughout rapid oxidation process, we have used detailed modeling of the heat loss, which for a reduce particle size and high temperatures (order of 2000 °C) is principally due to convection mechanism. We computed convective heat loss by using COMSOL software to find the rapid unsteady motion of the surrounding gas and the resulting heat outflow. The COMSOL multiphysics simulation platform helps to model and compute the process by defining geometry, meshing sample, specifying physics, solving, and then visualizing results.

### Nonlinear Cabrera-Mott Model

In the Cabrera-Mott model of metal oxidation [1-2, 17-18] aluminum ions have to tunnel through

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the ionization potential W to escape into the oxide layer. Such tunneling is assisted by a self-consistent electric potential V, created in the oxide layer by an imbalance of excess electrons $Ne^{\frac{eV}{k_BT}}$ and metal ions $Ne^{\frac{-eV}{kT}}$ near the metal-oxide interface; here N is the concentration of the charges far from the metal-oxidizer interface. The Poisson equation for V in the case of a spherically-symmetric particle is therefore

$$\nabla^2 V = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}V\right) = 8\pi k_0 eN\sinh\left(\frac{eV}{k_bT}\right), r_1 \leq r \leq r_2, \quad (1)$$

$$V(r_1) = V_0,$$

$$V(r_2) = 0.$$

Here $r_1$ is the metal particle radius, $(r_1 - r_2)$ is the oxide layer thickness, $k_0$ is the electrostatic constant, **e** is the elementary charge, $N = (n_e n_i)^{\frac{1}{2}}$, and $n_i$ and $n_e$ are given by $n_e = 2\left(\frac{2\pi m_e k_b T}{h^2}\right)^{\frac{3}{2}}\exp\left(-\frac{e\varphi}{k_bT}\right)$ and $n_i = N_i\exp\left(-\frac{eW_i}{k_bT}\right)$, where $m_e$ is the mass of electron, $k_b$ is the Boltzmann constant, h is a Plank constant, $N_i$ is the concentration of sites available for hopping metal ions. The physical meaning of $W_i$ is the difference of chemical potentials for metal ions in the metal and the oxide; $\varphi$ is the potential difference for electrons in the conduction bands of aluminum metal and the oxide (a semi-conductor); and the value of $V_0$ is determined from the condition that metal ion concentration at the interface with the oxide equals $n_i$. We have that

$$N = (n_e n_i)^{\frac{1}{2}} = N_0\left(\frac{T}{T_0}\right)^{\frac{3}{4}}\exp\left(-\frac{e(\varphi + W_1)}{2k_bT}\right),$$

$$N_0 = (2N_i)^{\frac{1}{2}}\left(\frac{2\pi m_e k_b T_0}{h^2}\right)^{\frac{3}{4}} \sim 1.5\times10^{27}\,\text{m}^{-3}, T\sim750\,\text{K}. \quad (2)$$

### Metal-Oxide Interface

The motion of the metal-oxide interface is due to the tunneling of metal ions through the ionization potential of the maximum height $W>W_i$. Electric field provides potential energy decrease for ion hopping from the bottom to the top of ionization potential, at a distance a~0.4 nm away. The normal velocity $u_n$ of the metal-oxide interface is directed towards the center and is therefore given by

$$u_n = \frac{dr_1}{dt} = -\Omega_1 nv\exp\left(-\frac{eW}{k_bT}\right)\exp\left(\frac{qea\,|\,V'(r_1)|}{k_bT}\right), \quad (3)$$

$$r_1(0) = r_{10}.$$

here $r_0$ is the initial metal sphere radius, which we assume to be $(25 - d)$ nm; where d is the initial oxide thickness, $\Omega_1 \approx 0.0166$ nm$^3$ is the volume of oxide per aluminum ion, n ~10 nm$^{-2}$ is the number of metal ions per unit surface area, v~$10^{12}$s$^{-1}$ is the frequency of tunneling attempts, and q = 3 is the aluminum valency.

In the Cabrera-Mott model, it's assumed that escaped metal ions migrate to the outer boundary of the oxide where they react with the oxygen, while the local Gibbs factor of excess densities of electrons and metal ions inside the oxide is essentially unaffected. Due to the spherical symmetry, the radius of the oxide-oxidizer interface $r_2$ changes uniformly, and can be found from conservation of the number of metal ions, taking into account difference in volumes per metal ion in the metal and the oxide,

$$\left(r_2^3 - r_{20}^3\right) = -k(r_1^3 - r_{10}^3).$$

Thus

$$r_2 = r_2(r_1)(r_{20}^3 + k(r_{10}^3 - r_1^3))^{\frac{1}{3}}, \ k \approx 0.386, \quad (4)$$

here $r_{20} = r_{10} + \delta$ where $\delta$~3 nm is the initial oxide layer thickness.

For small metal particles, it is important to take *self-heating* into account, due to heat released by exothermic aluminum oxidation, resulting in a temperature increase of the remaining metal and oxide layer. In [19], a simple self-heating model was used where temperature was computed based on reaction heat release and specific heats of reagents: assuming constant specific heats, and uniform temperature of nano-sized particle,

$$T \equiv T(r_1) = T_0 + \frac{\sigma h_{Al}\rho_{Al}\left(r_{10}^3 - r_1^3\right)}{c_{Al}\rho_{Al}r_1^3 + c_{Al_2O_3}\rho_{Al_2O_3}(r_2^3 - r_1^3)} \quad . \quad (5)$$

Here $\rho_{Al}$, $\rho_{Al_2O_3}$ are densities of the aluminum and oxide; $c_{Al}$, $c_{Al_2O_3}$ are specifics heats per unit mass; $H_{Al}$ is the oxidation reaction enthalpy per unit mass of aluminum, and $\sigma$ is the proportion of released heat which is used up for self-heating [8, 19]. We take the reaction initiation temperature $T_0$ = 750 K. Since $r_2$ can be found from $r_1$ using (4), the temperature T in (5) is determined by $r_1$. Due to high enthalpy release in aluminum oxidation (~24 kJ per gram of aluminum), adiabatic assumption $\sigma = 1$ yields unrealistically high maximum temperature, even when the melting and vaporization heats are taken into account. In [19], it was assumed that $\sigma = 0.11$ of the heat released contributes to self-heating, while the rest is lost due to radiation, heat conduction, and convection. For such value of $\sigma$, the maximum reaction temperature, corresponding to $r_1 = 0$, $r_2 = r_2$ (0) in (4), (5), will be $T_M \sim 2000$ °C, which agrees with experiment [8].

The power P, in watts, released as a result of the oxidation reaction is given by

$$P\left(\frac{m}{m_0}, T\right) = h_{Al}m_0\frac{d}{dt}\left(\frac{m}{m_0}\right) = 4\pi r_1^2 h_{Al}\rho_{Al}\Omega_1 n_2 \nu \exp\left(-\frac{eW}{k_bT}\right)\exp\left(\frac{qea\,|\,V'(r_1)\,|}{k_bT}\right), \quad (6)$$

where $h_{Al} \sim 24$ kJ/g is the aluminum oxidation enthalpy, $\rho_{Al}$ is aluminum density, $m_0 = \frac{4\pi}{3}(r_{10}+d)^3\rho_{Al}$ is initial mass of the particle, d is initial oxide layer thickness, and $m = \frac{4\pi}{3}r^3\rho_{Al}$. Thus P can be found by solving the equation for the potential (1) for different temperatures T and radii $r_1$. This computation was performed in [19], where we have computed a related quantity

$$L\left(\frac{m}{m_0}, T\right) = \log_{10}\frac{d}{dt}\left(\frac{m}{m_0}\right). \quad (7)$$

Thus,     $P\left(\frac{m}{m_0}, T\right) = h_{Al}m_0 10^{L\left(\frac{m}{m_0}, T\right)}. \quad (8)$

In Ref. 19 a simple self-heating was used, assuming that a certain fixed proportion of released heat is used for self-heating; that proportion was matched to experimentally known maximal temperature.

### Numerical Modeling of Self-Heating

Oxidation reaction power P in the Cabrera-Mott model with a self-consistent potential for an aluminum particle of radius 25 nm, as a function of oxidized metal mass, at various temperatures is presented in Fig 1. During oxidation of a small particle, its temperature does not stay constant since energy is released as a result of highly exothermic oxidation reaction. To determine oxidation dynamics (1) and (3) a self-heating model is needed to find the temperature as a function of $r_1$ in (5).
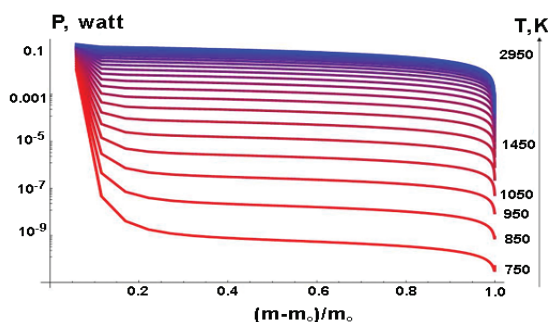


Fig. 1. Oxidation reaction power P [watts] in Cabrera-Mott model with a self-consistent potential for an aluminum particle of radius 25 nm, as a function of oxidized metal mass, at various temperatures. Ionization parameters used in the model: $V_0 = 0.65$ V, $\phi + W_i = 1.5$ V, $W = 1.7$ V, $a = 0.4$ nm.

We have investigated a more accurate self-heating model of particle oxidation based on balance of energy released as a result of chemical reaction and lost due to convection and radiation,

$$c_v m_0 \frac{dT}{dt} = P - \dot{q}_{conv} - \dot{q}_{rad}, \quad (9)$$

where $c_v m_0 \frac{dT}{dt}$ is the heat transfer to the particle per second, and $\dot{q}_{conv}, \dot{q}_{rad} = 4\pi\sigma_b r_2^2 T^4$, is the loss of energy per second due to convection and radiation (here $\sigma_b$ is the Stefan-Boltzmann constant). As a numerical experiment, we have used the COMSOL software to model *non-stationary* convection in the air and to find the time dependence of the temperature and metal radius. Result of this computation is presented in Fig. 2. Overall oxidation time scale in COMSOL computation was of order $10^{-5}$ s, as in the simple experiment – matched oxidation model considered in [19] and these results are compatible with experimentally available data [8, 20]. We note that in our range of parameters, radiation term is smaller that convection.
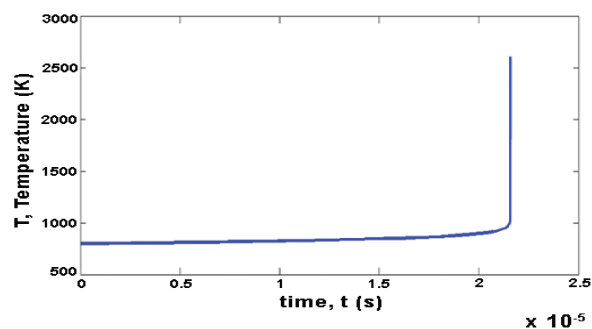


Fig. 2. Temperature as a function of time, for the case of spherical aluminum nanoparticle of initial radius of $r_{10} = 23$ nm, with initial oxide thickness d = 2 nm.

We note that in the stationary regime convection in the case of small particle can be modeled by Newton's law [21-23],

$$\dot{q}_{conv} \cong \frac{k}{r_2}\left(4\pi r_2^2\right)(T - T_\infty), \quad (10)$$

where $T_\infty$ is the ambient temperature, and k, [Wm$^{-1}$K$^{-1}$], is the air's thermal conductivity. We have investigated numerically using the simplified convection

terms given by Newton's law in (9). We observed that in such kind of computation, total energy lost to convection during rapid phase of oxidation ($10^{-8}$ s) will be of the same order as the total energy released. However, it is hard to achieve a tight balance between the power released by oxidation and lost in convection. In the simplified convection model, for sufficiently small initial oxide thickness (of order 1 nm), and sufficiently high initiation temperatures (of order 800 K and above), $P >> \dot{q}_{conv}$ throughout the reaction time, so the exothermic reaction wins and oxidation occurs very quickly reaching very high (and physically quite unrealistic) temperatures. For thicker initial oxide layer or lower initial temperature, the convection dominates and the self-heating mechanism remains suppressed; in that case oxidation time scale is much larger [20]. Similar behavior was observed in [2] using modified Newton's law model.

We have attempted a more accurate self-heating model of particle oxidation based on a balance of energy released as a result of the chemical reaction and lost due to convection. We have used the COMSOL 4.3 software in this study to model heat transfer, using COMSOL heating module. Our set-up in this computation was as follows. We have placed a solid aluminum ball of radius $R_{in} = 25$ nm at the origin, surrounded by a concentric control sphere of radius $R_{out} = 1500$ nm filled with air. The initial temperature of the aluminum ball was taken to be $T_{in} = 800$ K. Slip boundary condition for the air velocity was used at the air-metal boundary. The boundary condition at the outer sphere was the open boundary condition with zero normal stress, but otherwise allowing air to move through the outer sphere, and with the outside temperature taken to be $T_{out} = T_{in} = 800$ K. We have added viscous heating and pressure work options in COMSOL to the default conjugate heat transfer set-up for a careful modeling of the heat transfer in the air. We have also added gravity volume force in the air to enable convective air movement. A physics-controlled mesh was used in the study to add boundary mesh layers as appropriate.

A non-stationary 3D solver was used in our modeling. To model aluminum oxidation chemical reaction itself, we have added a surface heat source with surface density $\frac{P(\frac{m}{m_0}, T)}{4\pi R_{in}^2}$ on the air-metal boundary, using interpolated data to get $P\left(\frac{m}{m_0}, T\right)$, and introducing an extra boundary ODE on the air-metal boundary in order to estimate $\frac{m}{m_0}$. The extra ODE was computing the total energy Q released, based on instantaneous energy flow $w_Q \equiv \dot{Q}$, computed by the COM-

SOL time-dependent solver. Thus $\frac{m}{m_0} = \frac{Q}{Q_{tot}}$, where $Q_{tot} = h_{al}m_0$ and Q is a solution of ODE $\dot{Q} = w_Q$. The initial oxide thickness d was accounted for via an initial condition for the latter ODE:

$$Q(0) = (1 - (\frac{r_{10}}{r_{10} + d})^3)Q_{tot}. \tag{11}$$

The chemical reaction heat source was switched off once all the available energy was used and $Q \geq Q_{tot}$; that was enforced by multiplying $P(\frac{m}{m_0}, T)$ by an appropriate step function.

The results of our computation of the temperature as a function of time, for the case of spherical aluminum particle of initial radius $r_{10} = 23$ nm, with initial oxide thickness d = 2 nm are shown in Fig. 2. The calculation indicates that enormous temperature rise generated at about $2.3 \times 10^{-5}$ s that increases very quick temperature of nanoparticle up to 2600 K. This calculation also demonstrates estimation of ignition delay time that was about $2.3 \times 10^{-5}$ s. Overall oxidation time scale computed using detailed convection modeling in COMSOL is compatible with the simpler self-heating mechanism considered in [19]. These computed data will be useful for future computation of the array of the nanoparticles to simulate combustion of several nanoparticles.

## Conclusions

The oxidation model of nanoparticle of aluminum was investigated numerically by using COMSOL multiphysics software. We have investigated the Cabrera-Mott model with the self-consistent potential to find oxidation reaction power for nanostructured aluminum particle as a function of temperature and the oxidized proportion of the metal mass. Our results together with a self-heating model enable us to find time dependence of metal particle radius and temperature. Matching maximal temperature to experiment as well as numerical modeling of non-stationary convective heat loss in COMSOL provides roughly the same oxidation time scale compatible with the previous experimental data in [8, 20]. Simplified convection models using Newton's law suggests a very sharp pyrophoric threshold for oxide thickness/initiation temperature.

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