

# Spherically symmetric oxidation model of aluminum nanoparticles

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## ABSTRACT

Kinetics of oxidation of metal nanoparticles acquired practical importance with rapidly developing nanoenergetic systems and materials. Nanoenergetic thermites include mixtures of Al and metal oxides in nanoscale. Our research focuses on modeling aluminum combustion in nanoscale. The research problem is considered a spherically symmetric case and used the Cabrera Mott oxidation model to describe the kinetics of oxide growth on the aluminum nanoparticles to predict reaction temperature, thermal front velocity and oxidation time. We assumed that aluminum of radius 10 to 50 nm is covered by a thin oxide layer (1-4nm) and is surrounded by abundant amount of oxygen stored by oxidizers. The ball is rapidly heated up to ignition temperature to initiate self-sustaining oxidation reaction as a result of highly exothermic reaction. We investigated oxidation model numerically, using the COMSOL software. The software runs the finite element analysis along with the grid takes into account the geometric configuration of the body. In the oxide layer of excess concentrations of electrons and ions are dependent on the electric field potential with the corresponding of the Gibbs factors and that it conducts to the solution of a nonlinear Poisson equation for the electric field potential in a moving boundary domain.

**Keywords:** Nanoenergetic Thermites, Aluminum, Cabrera Mott model, Oxidation.

## 1 INTRODUCTION

Many previous studies examined the mechanism and kinetics of aluminum particle oxidation [1-9]. Oxidation of aluminum yields high enthalpy release and has been extensively used for propulsion, pyrotechnics and explosion reactions [10, 11]. Nanoenergetic materials (NM) based on aluminum thermites may store two times more energy per volume than conventional monomolecular energetic materials [12]. 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 [13]. Among numerous thermodynamically feasible Metastable Intermolecular Composites mixtures the most widely investigated are Al/Fe<sub>2</sub>O<sub>3</sub>, Al/MoO<sub>3</sub>, Al/WO<sub>3</sub>, Al/CuO, Al/Bi<sub>2</sub>O<sub>3</sub> and Al/I<sub>2</sub>O<sub>5</sub> nano systems [14-20].

Our recent experiments suggest that oxidation of nanoparticles of aluminum with Bi<sub>2</sub>O<sub>3</sub> and I<sub>2</sub>O<sub>5</sub> occurs in a few microseconds or less [17-19]. Rapid reaction in the nanostructured thermites cannot be explained by a conventional mechanism based on the diffusion of Al and O atoms in oxides.

Nonlinearity in equation for the self-consistent electric potential, together with the self-heating effect, leads to significant increase of oxidation rate for nano-sized aluminum particles, compared to the model with Coulomb potential and without self-heating. Results of our modeling suggest oxidation time scales in microseconds range for nano-sized aluminum particles, in agreement with the experimental evidence [12]. Despite the significant development and progress in the studies of nanothermite reaction, many reaction mechanisms and reaction features haven't been thoroughly studied yet, and many potential applications have not been explored.

In this report, we investigate a rapid oxidation model of spherical aluminum nanoparticles surrounded by oxygen, using the Cabrera-Mott oxidation model [7-9] 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 temperature. To find the temperature of the nanosized particle throughout rapid oxidation process, we have used detailed modeling of the heat loss, which for a nanosized particle and temperatures of order 2000<sup>0</sup> C is principally due to convection. 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 process by defining geometry, meshing sample, specifying physics, solving, and then visualizing results.

## 2 CABRERA-MOTT MODEL

In the Cabrera-Mott model of metal oxidation [1-4, 7] aluminum ions have to tunnel through 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  $N e^{\frac{eV}{k_B T}}$  and metal ions  $N e^{\frac{-eV}{k_B T}}$  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

$$\nabla^2 V = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} V \right) = 8\pi k_0 \mathbf{e} N \sinh \left( \frac{eV}{k_b T} \right),$$

$$r_1 \leq r \leq r_2$$

$$V(r_1) = V_0$$

$$V(r_2) = 0 \quad (1)$$

Here  $r_1$  is the metal particle radius,  $(r_1 - r_2)$  is oxide layer thickness,  $k_0$  is the electrostatic constant,  $\mathbf{e}$  is the elementary charge,  $N = (n_e n_i)^{\frac{1}{2}}$ , and  $n_i$  and  $n_e$  are given by

$$n_e = 2 \left( \frac{2\pi m_e k_b T}{h^2} \right)^{\frac{3}{2}} \exp \left( -\frac{e\phi}{k_b T} \right),$$

$$n_i = N_i \exp \left( -\frac{eW_i}{k_b T} \right),$$

where  $m_e$  is the mass of electron,  $k_b$  Boltzman constant,  $h$  - 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;  $\phi$  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

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

$$N_0 = (2N_i)^{\frac{1}{2}} \left( \frac{2\pi m_e k_b T_0}{h^2} \right)^{\frac{3}{4}} \sim 1.5 \times 10^{27} \text{ m}^{-3},$$

$$T_0 \sim 750 \text{ K}. \quad (2)$$

### 3 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  $a \sim 0.4$  nm away. The normal velocity  $u_n$  of the metal-oxide interface is directed towards the center and is therefore given by

$$u_n = \frac{dr_1}{dt}$$

$$= -\Omega_1 n v \exp \left( -\frac{eW}{k_b T} \right) \exp \left( \frac{qea|V'(r_1)|}{k_b T} \right)$$

$$r_1(0) = r_{10}. \quad (3)$$

Here  $r_{10}$  is the initial metal sphere radius, which we assume to be  $25 - d$  nm; where  $d$  is the initial oxide thickness,  $\Omega_1 \approx -0.0166 \text{ nm}^3$  is the volume of oxide per aluminum ion,  $n_2 \sim 10 \text{ nm}^{-2}$  is the number of metal ions per unit surface area,  $v \sim 10^{12} \text{ s}^{-1}$  is the frequency of tunneling attempts, and  $q = 3$  is the aluminum valency.

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,

$$(r_2^3 - r_{20}^3) = -k(r_1^3 - r_{10}^3), k \approx 0.386$$

Thus,

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

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

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

$$P \left( \frac{m}{m_0}, T \right) = h_{Al} m_0 \frac{d}{dt} \left( \frac{m}{m_0} \right)$$

$$= 4\pi r_1^2 h_{Al} \rho_{Al} \Omega_1 n_2 v \exp \left( -\frac{eW}{k_b T} \right) \exp \left( \frac{qea|V'(r_1)|}{k_b T} \right) \quad (4)$$

where  $h_{Al} \sim 24$  kJ/g is aluminum oxidation enthalpy,  $\rho_{Al}$  is aluminum density,  $m_0 = \frac{4\pi}{3} (r_0 + d)^3 \rho_{Al}$  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  $r_1$ . We have previously computed a related quantity

$$L \left( \frac{m}{m_0}, T \right) = \log_{10} \frac{d}{dt} \left( \frac{m}{m_0} \right) [21],$$

thus

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

In [21], 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.

#### 4 SELF-HEATING MODEL OF PARTICLE OXIDATION

In this report, we attempt 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. We have used the COMSOL software in this study to model convection. Our set-up for this computation was as follows. We have placed a solid aluminum ball of radius  $R_{in} = 25nm$ . at the origin, surrounded by a concentric control sphere of radius  $R_{out} = 1500 nm$  filled with air. Initial temperature of the aluminum ball was taken to be  $T_{in} = 800K$ . Slip 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  $T_{out} = T_{in} = 800K$ .

We have added viscous heating and pressure work options 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. Physics-controlled mesh was used in the study to add boundary mesh layers as appropriate.

Nonstationary 3d solver was used in our modeling. To model chemical reaction itself, we have added a surface heat source with density  $\frac{P(\frac{m}{m_0}, T)}{4\pi r_0^2}$  on the air-metal boundary, using interpolated data to get  $P(\frac{m}{m_0}, T)$ , and introducing an extra boundary ODE on the air -metal boundary in order compute  $\frac{m}{m_0}$ . The extra ODE was simply computing the total energy  $Q$  which escaped from the metal into the surrounding air, based on instantaneous energy flow  $W_Q \equiv \dot{Q}$  through a sphere surrounding the metal particle. The energy flow  $W_Q$  could be readily computed in COMSOL using an instantaneous surface integration.

Thus  $\frac{m}{m_0} = \frac{Q}{Q_{tot}}$ , where  $Q_{tot} = h_{Al}m_0$ , and  $Q$  is a solution of ODE  $\dot{Q} = W_Q$ . Initial oxide thickness  $d$  was accounted for via an initial condition for the latter ODE:  $Q(0) = (1 - (\frac{r_0}{r_0+d})^3)Q_{tot}$ . 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 are shown in Figure 1. Overall oxidation time scale computed using detailed convection modeling in COMSOL is compatible with the simpler self-heating mechanism considered in [21].

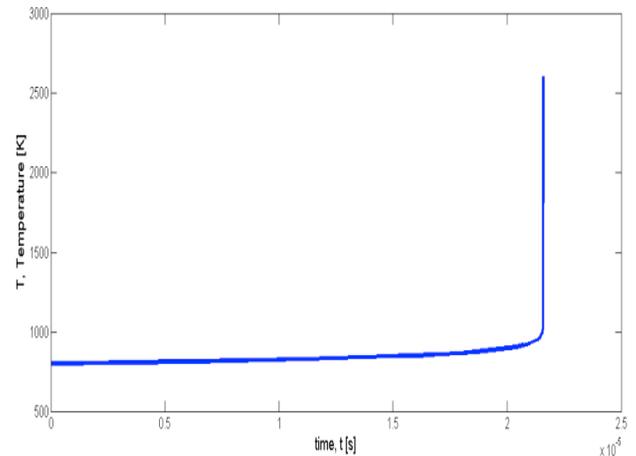


Figure 1. Temperature as a function of time, for the case of spherical aluminum particle of radius  $r_0 = 23 nm$ , with initial oxide thickness  $d = 2 nm$ . Initial temperature and the outside temperature are taken to be 800 K.

#### 5 SUMMARY

The oxidation model of nanoparticle of aluminum was investigated numerically by using COMSOL software. The result of overall oxidation time compatible with the simpler self-heating mechanism and experimental results.

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