

# Rapid oxidation and self-heating model of aluminum spherical nanoparticles

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## ABSTRACT

Nanostructured highly-exothermic reactive mixtures, referred to as Nanoenergetic Materials or Metastable Intermolecular Composites, may release energy much faster than conventional energetic materials. The size reduction of reactant powders such as aluminum from micro- to nano-size increases the reaction front propagation velocity in some systems by two to three orders of magnitude. Our recent experiments suggest that oxidation of nanoparticles of aluminum occurs in a few microseconds. In this report, we present a rapid oxidation model of spherical aluminum nanoparticles surrounded by oxygen, using Cabrera-Mott oxidation model with self-consistent potential, and taking self-heating into account. In this model, aluminum ions are helped to escape aluminum surface (overcoming ionization potential  $W_i$ ), and to move through oxide layer to its outer part with the help of self-consistent electric field potential ( $V$ ) created by the imbalance between excess positive aluminum ions and electrons. Excess concentrations of electrons and ions in oxide layer in turn are dependent on electric field potential via appropriate Gibbs factors, leading to a self-consistent version of Poisson equation. In contrast with the Coulomb potential, our result shows that for aluminum nanoparticles (less than 100 nm in diameter), a double layer potential and self-heating lead to enhanced oxidation rates throughout the oxidation process.

**Keywords:** nanoenergetic thermite materials, aluminum nanoparticles, Cabrera-Mott oxidation model, self-heating and increased reaction rate, double layer, moving interface .

## 1 INTRODUCTION

Major progress has been made during the past two decades in developing advanced energetic materials (EM) that can rapidly release temperature and pressure waves, and they have extensive military and civil potential applications in propellants, explosives, and pyrotechnics. The development of novel EM, their design, synthesis and fabrication procedures are critical for national security and it was recognized as a significant addition to support of changing force structure for advanced weapons platforms. Nanostructured highly-exothermic reactive mixtures, referred to as Nanoenergetic Materials (NM) or Metastable Intermolecular Composites (MIC), may release energy much faster than conventional EM

[1]. Well established nanoenergetic thermite reactions include those of mixtures of Al and metal oxides. Among numerous thermodynamically feasible MIC 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 and Al/Bi<sub>2</sub>O<sub>3</sub> nano systems [2]. 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. Recent advances in the integration of nanoenergetic components into micro-electro-mechanical systems (MEMs) imply a possible development of "nanoenergetics-on-a-chip" devices, which can have potential applications in micro-propulsion systems.

The size reduction of reactant powders such as aluminum from micro- to nano-size increases the reaction front propagation velocity in some systems by two to three orders of magnitude. 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 [3-6]. There are several advantages, which can be accomplished by using Al/Bi<sub>2</sub>O<sub>3</sub> and Al/I<sub>2</sub>O<sub>5</sub> nanocomposites: (i) reduced ignition delay and reaction times; (ii) superior heat transfer rates; (iii) tunability of novel energetic fuel/propellants with desirable physical properties; (iv) enhanced density impulse; (v) incorporating nanoenergetic materials into the MEMs and NEMs systems [3]. In this report, we present a rapid oxidation model of spherical aluminum nanoparticles surrounded by oxygen, using Cabrera-Mott oxidation model [7] with a self-consistent potential, and taking self-heating into account.

## 2 CABRERA-MOTT OXIDATION MODEL

In the Cabrera-Mott model of metal oxidation, aluminum ions are helped to escape aluminum surface (overcoming ionization potential  $W$ ), and to move through oxide layer to its outer part with the help of self-consistent electric field potential  $V$ , created by imbalance between excess positive aluminum ions and electrons. In the Cabrera-Mott model, reaction with oxidizer happens on the outer part of oxide layer once aluminum ions are getting in contact with the oxidizer and react. Excess concentrations of electrons and ions in oxide layer in turn are dependent on electric field potential  $V$  via appropriate Gibbs factors, leading to a self-consistent version of Poisson equation. In the spherically-symmetric case this equation is given by (1).

The normal velocity field of the moving boundary of the metal is due to escape of metal ions, and is assisted by the potential gain in the electric field potential, appearing as a Gibbs factor in (5).

The rate of growth of the outer layer of the oxide is proportional to the metal ion current, and taking into account the difference in volumes per aluminum atom in the metal and in the oxide. In the spherically symmetric case, the rate of growth of the outer layer is uniform.

Moving interface equations (5), but with the Coulomb potential rather than the self-consistent potential solving the Poisson/sinh-Gordon Eq. (1), and without the self-heating effect (4), were considered in [10].

### 3 CABRERA-MOTT MODEL: SPHERICALLY SYMMETRIC CASE

To estimate reaction times, we assume that a ball of aluminum of radius 20 to 50 nm. is covered by a thin oxide layer, and is surrounded by abundant quantities of oxygen outside. The ball is rapidly heated to temperature  $T_0$ , sufficient to initiate very fast oxidation reaction, further boosted by self-heating as a result of oxidation. We assume spherical symmetry of the problem.

#### 3.1 Self-Consistent Poisson Equation

Electric field potential  $V$  is induced in the oxide layer due to the difference in chemical potentials of the metal and oxidizer. In the framework of Cabrera-Mott model [7], we assume the Gibbs distribution of concentration of excess electrons and metal ions in the oxide film, and arrive at the self-consistent Poisson equation for the potential  $V$ :

$$\begin{aligned} r_1 \leq r \leq r_2, \\ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} V \right) - 8\pi k_0 e N \sinh \left( \frac{eV}{k_b T} \right) = 0, \\ V(r_1) = V_0 \\ V(r_2) = 0, \\ N = (n_e n_i)^{1/2}. \end{aligned} \quad (1)$$

Here  $n_i$  and  $n_e$  are concentrations of respectively aluminum ions and of excess electrons in the oxide layer, as in Eq. (6) in reference [7],

$$\begin{aligned} n_e &= 2 \left( 2\pi m_e k_b T / h^2 \right)^{3/2} \exp \left( - \frac{e\phi}{k_b T} \right), \\ n_i &= N_i \exp \left( - \frac{eW_i}{k_b T} \right). \\ k_0 &= 8.99 * 10^9 \frac{\text{N m}^2}{\text{C}^2}, \\ e &= 1.60 * 10^{-19} \text{C}. \end{aligned} \quad (2)$$

Here  $m_e$  is the mass of electron,  $k_b$  Boltzman constant,  $h$  Plank constant,  $N_i$  is the concentration of sites available for hopping metal ions. Note that

$$\begin{aligned} N &= N_0 \left( \frac{T}{T_0} \right)^{3/4} \exp \left( - \frac{e(\phi + W_i)}{2k_b T} \right), \\ N_0 &= (2N_i)^{1/2} \left( 2\pi m_e k_b / h^2 \right)^{3/4} \sim 1.53 \times 10^{27} \text{ m}^{-3} \text{ at} \\ &T_0 \sim 750 \text{K}. \end{aligned}$$

The physical meaning of  $W_i$ , in electron-volts, 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 ion concentration at the interface with oxide equals  $n_i$ . However in a phenomenological model like Cabrera-Mott, those ionization potentials may be considered as model parameters (see discussion in [8,9]).

Suppose that initial radius of the metal ball is  $r_{10}$ , and of the ball together with initial oxide layer  $r_{20} = r_{10} + \delta$ ,  $\delta \sim 1-2$  nm. As the metal ball oxidizes, its radius  $r_1$  becomes smaller. The ratio of expected total number of excess aluminum ions in the oxide layer bulk to the total number of oxidizing ions is a very small number, so in effect we can assume that an equal number of ions escape the metal surface and oxidize on the outer surface of the oxide layer. Therefore the radius of the ball together with oxide layer can be found from the conservation of number of aluminum ions, and taking into account the ratio of volumes of aluminum atom and of the aluminum oxide molecule,  $0 = (r_2^3 - r_{20}^3) + \kappa (r_1^3 - r_{10}^3)$ , thus  $r_2$  is a function of  $r_1$ . We can assume that the oxide layer and metal always stay in mechanical contact, so the interface between them is the shrinking aluminum ball surface. Using known volumes per aluminum atom in the metal and oxide, we get

$$r_2 \equiv r_2(r_1) = (r_{20}^3 + \kappa (r_{10}^3 - r_1^3))^{1/3}, \kappa \approx 0.386. \quad (3)$$

#### 3.2 Self-Heating

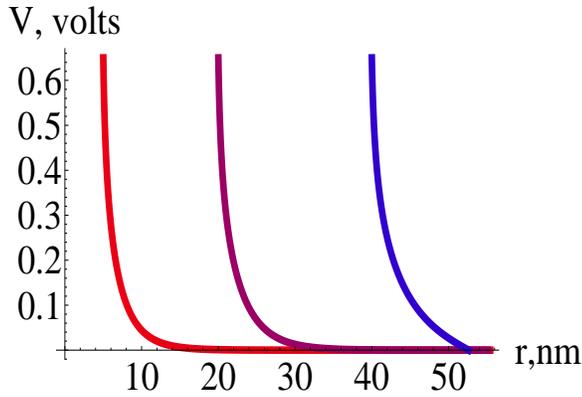
Heat released in the reaction will heat up the remaining metal and the oxide layer. Taking such self-heating into account,

$$T \equiv T(r_1) = T_0 + \frac{H_{Al} \rho_{Al} (r_{10}^3 - r_1^3)}{c_{Al} \rho_{Al} r_1^3 + c_{Al_2O_3} \rho_{Al_2O_3} (r_2^3 - r_1^3)}. \quad (4)$$

Here  $\rho_{Al}$ ,  $\rho_{Al_2O_3}$  are densities of the aluminum and oxide,  $c_{Al}$ ,  $c_{Al_2O_3}$  are specific heats per unit mass, and  $H_{Al}$  is the oxidation reaction enthalpy per unit mass of aluminum.

We take reaction initiation temperature  $T_0$  to be  $\sim 750 \text{K}$ . Since  $r_2$  can be found from  $r_1$  (3), the temperature  $T$  in (4) is determined by  $r_1$ .

We found the self-consistent potential  $V$ , by solving numerically the boundary value problem for the Poisson equation (1) for various radii  $r_1$ . Our results are illustrated in Figure 1. The values of ionization potentials  $V_0$ , ( $\phi + W_i$ ) are estimated from the data in the Cabrera-Mott paper [7].



**Figure 1:** Self-consistent potential  $V$  for  $r_1 = 5, 20, 40$  nm. Here  $V_0 = 0.65$  V,  $\phi + W_i = 1.6$  V,  $T_0 = 750$  K.

### 3.3 Moving Interface

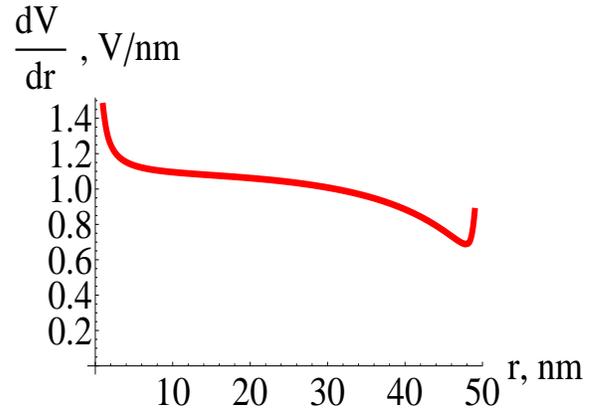
In the Cabrera-Mott model, the oxidation of metal occurs via tunneling of aluminum ions into the oxide layer, overcoming ionization potential of maximal height  $W > W_i$ , and assisted by the self-consistent electric potential. Electric potential provides potential energy gain while hopping from the bottom to the top of ionization potential, at a distance  $\alpha_0$  away. It is further assumed that escaped ions eventually migrate to the outer boundary of the oxide where they react with the oxygen, while local Gibbs distribution of excess densities of electrons and metal ions inside the oxide is unaffected. This leads to the equation for the inner metal radius

$$\begin{aligned} \frac{dr_1}{dt} &= -\Omega_1 \nu n_2 \exp\left(\frac{-eW}{kT}\right) \exp\left(\frac{qe\alpha_0|V'(r_1)|}{k_bT}\right), \\ r_1(0) &= r_{10}, \\ r_2(0) &= r_{20} = r_{10} + \delta, \quad \delta \sim 1 - 2 \text{ nm}, \\ r_{10} &\text{ is initial radius of metal ball, } \sim 20 - 50 \text{ nm}, \\ \alpha_0 &\sim 0.35 \text{ nm}, q = 3. \end{aligned} \quad (5)$$

Here the volume per aluminum ion  $\Omega_1 \approx 0.0166 \text{ nm}^3$ , atomic frequency  $\nu \sim 10^{12} \text{ s}^{-1}$ , number of ions per unit surface area  $n_2 \sim 10 \text{ nm}^{-2}$ .

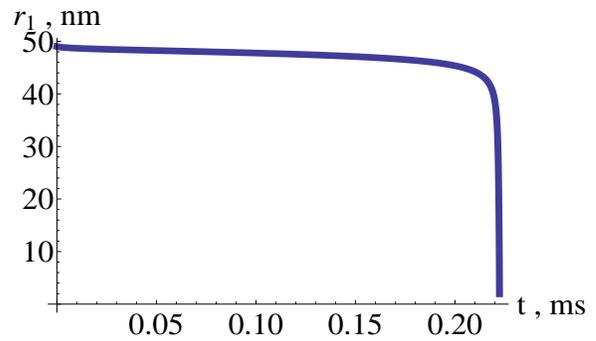
Eq. (5) is similar to the model of metal ball oxidation considered in [10] but with a different potential (a solution of the self-consistent Poisson equation (1) rather than the Coulomb potential), and with the self-heating effect taken into account. Here we use the value of  $\alpha_0$  from the Cabrera-Mott paper [7].

The gradient of the potential on the metal surface can be computed by solving (1) for various radii  $r_1$ . Our results are presented in Figure 2.



**Figure 2:** Gradient of the self-consistent potential on the metal boundary, as a function of metal radius, and taking self-heating into account. Here  $V_0 = 0.65$  V,  $\phi + W_i = 1.6$  V,  $T_0 = 750$  K.

Using results for the gradient of the potential on metal boundary, we can find the radius of the metal ball as a function of time by solving the Eq. (5). Our results are shown in Figure 3.



**Figure 3:** Oxidation time scales: metal radius  $r_1$  as a function of time,  $W = 1.8$  V,  $T_0 = 750$  K.

## CONCLUSIONS

Nonlinearity in the equation for the self-consistent electric potential, giving a double-layer type solution on the metal-oxide interface, together with the self-heating effect, produce a dramatic increase of oxidation rate for nano-sized aluminum balls (e.g. compared to time scales in the model with Coulomb potential and no self-heating). Results for oxidation time scale are very sensitive to values of ionization potentials, since they appear as Gibbs factors in the boundary velocity. Therefore we expect that oxidation rate will be very sensitive to defects, and to deviation from spherical symmetry.

## ACKNOWLEDGMENTS

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## NOMENCLATURE

$V$  the electric field potential in the oxide (volts),  $T$  the temperature (K),  $t$  time;

$r$  a radius in the spherical coordinates;  $r_1$  the radius of the metal ball,  $r_2$  the outer radius of the oxide shell;  $r_{10}$  and  $r_{20}$  the initial values of those;

$W_i$ ,  $W$ , ionization potential for ions, and the maximal potential, to move aluminum ions from the metal to the oxide;

$\phi$  the potential to move an electron from the metal into the conduction band of the oxide;

$n_i$  concentration of metal ions in the oxide,  $n_e$  concentration of excess electrons in the oxide,  $N = (n_e n_i)^{1/2}$ .

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