

A molecular dynamics simulation on the oxidation of core-shell aluminum nanoparticles in oxygen and water environments

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Abstract

The oxidation mechanisms of core-shell aluminum nanoparticles (ANPs) in high-temperature steam and oxygen are investigated by ReaxFF molecular dynamics (MD) simulation. The details concerning reaction heat release, heat transfer, atomic diffusion process, and ANP structure evolution are studied by examining the temporal variations of temperature, energy, atoms concentration distributions and particle structure, respectively. The atomic-level heat and mass transfer processes reveal that for both ANP/H₂O and ANP/O₂ systems, at the initial stage of oxidation, the heat transfer between ANP and environmental oxidizer is dominant. Thereafter, the reaction plays an increasingly significant role. The heat transfer efficiency of ANP/H₂O is higher than that of ANP/O₂, while the reaction exotherm of ANP/H₂O is lower than ANP/O₂. The final particle temperature for ANP/O₂ system is much higher than that of ANP/H₂O. The diameter of the former is also larger. During the oxidation of ANP, the core Al atoms diffuse outward into the oxide shell, which pushes the shell Al atoms outward and results in the expansion of ANP. The shell O atoms diffuse inward and left a vacant lattice site, through which the ambient H and O atoms diffuse into the oxide shell.

1 Introduction

The aluminum nanoparticle has been widely utilized in explosives and power generation due to its excellent energetic properties. Considerable efforts have been made to study the oxidation mechanism of aluminum nanoparticle in air [1, 2]. However, during the oxidation of aluminum, the Al typically reacts with combustion products of the oxidizer, such as H₂O and CO₂ [3]. It is also reported that the Al-H₂O reaction has become an attractive source of hydrogen [4]. Therefore, it's important to explore the mechanism of aluminum-water reaction. Recently, significant efforts have been taken to study the reaction of aluminum and water. Risha et al. [5] investigated the combustion behavior of nano-aluminum and liquid water. They found that the flame temperature of Al/water mixture is lower than the Al/air mixture, and the combustion initially proceed through a surface reaction. Sundaram et al. [6] studied the flame propagation of aluminum-ice mixtures over a pressure range of 1-10 MPa. The results showed the burning rates have an

exponential dependent with pressure and the combustion of aluminum-ice mixtures is controlled by diffusion processes across the oxide layers of particles.

Due to extremely short reaction time and particle aggregation during ANPs oxidation, it is difficult to experimentally investigate detailed process of aluminum oxidation reaction. Molecular dynamics (MD) simulation has been employed to provide insights into oxidation mechanism of ANPs with oxygen. Zeng and Cheng [7] performed MD simulations to study the atomic diffusion behaviors of core-shell ANPs during heating process. They reported that the diffusivities of core Al atoms and shell O atoms at the core-shell interfaces decreased by increasing the shell thickness after heating. In our previous work, the combustion of ANP/O₂ under different temperature and pressure was investigated and the whole process was divided into four stages [8]. However, there are few MD studies on the oxidation of ANP/H₂O systems. Russo et al. [9] employed ReaxFF MD to examine the dissociation of absorbed water on an aluminum nanocluster. But their model didn't take the effect of oxide shell into account.

In this paper, the oxidation mechanisms of core-shell aluminum nanoparticle with water and oxygen were investigated at atomic scale; their differences in reaction, heat transfer and ANP structure were compared. By comparing the variation of temperature, energy, ANP structure, atoms concentration distributions, the dynamics associated with the oxidation of core-shell ANP in oxygen and water environments were examined. This study will provide insights into the thermal transfer and reaction mechanism of ANP oxidation reaction.

2 Method

2.1 Simulation Details

The reactive force field (ReaxFF) was adopted to simulate the oxidation of ANP with O₂ and H₂O. ReaxFF is a general bond-order based force field, which is parameterized against quantum mechanics (QM) based training sets and able to describe the bond formation and breaking which cannot be achieved by conventional MD methods. It has proved that the ReaxFF is more accurate than most of the semi-empirical methods; furthermore, it is computationally much cheaper than the density functional theory (DFT), allowing simulations in larger systems and longer physical time. The Al/C/H/O ReaxFF parameters used in this paper have been trained and validated by Hong et al. [10].

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ReaxFF MD simulations are conducted with the LAMMPS package [11].

The core-shell ANP is firstly prepared. The Al core with 6 nm-diameter was obtained by cutting bulk face-centered cubic (FCC) Al. The amorphous oxide shell of 1 nm thickness was cut from the annealed alumina. The core-shell ANP was obtained by combining the Al core and the oxide shell together. Then the obtained ANP was thermalized under NVT to form a stable core-shell interface. Subsequently, the ANP was put into an environment consisting of oxygen or water molecules at 2000K. The system was then simulated under NVE for 160 ps to examine the oxidation of the ANP. Periodic boundary conditions were implemented in all three directions.

Figure 1 shows the initial configuration of ANP at the beginning of combustion process in water environment. The ANP with a temperature of 300 K locates within $R \leq 4$ nm, while the ambient gas molecules with $T = 2000$ K at $R > 5$ nm. ReaxFF MD simulations were conducted using micro-canonical ensemble.

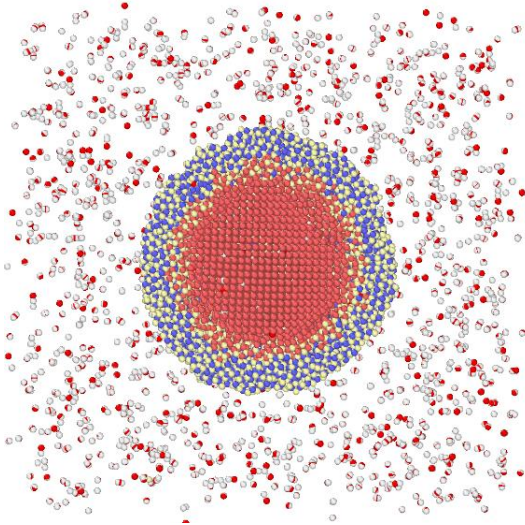


Figure 1: Cross-section snapshot of initial configuration for an aluminum nanoparticle in 2700 water molecules.

2.2 Heat transfer and reaction exotherm

Both heat transfer and reaction between ANP and oxidizer contributed to the particle temperature increase dT_p

$$dT_p = \frac{3}{2k_B} dKE_p = \frac{3}{2k_B} (E_r + E_t) \quad (1)$$

where dKE_p is the kinetic energy variation of ANP atoms, k_B is the Boltzmann constant, and E_t and E_r are the contributions of heat transfer and reaction. Then we have

$$dKE_p = E_r + E_t \quad (2)$$

The contributions of heat transfer and reaction between ANP and oxidizers are analyzed by the kinetic energy variations of ANP and environmental oxidizers. The E_t is calculated as

$$E_t = -dKE_e \quad (3)$$

where dKE_e is the kinetic energy variation of environmental oxidizer atoms. Combining Eq. (2) with (3), the E_r is calculated as

$$E_r = dKE_p + dKE_e \quad (4)$$

To distinguish the atoms from ANP and oxidizer, two methods are used in this paper. In Method 1, atoms in ANP and oxidizer are marked before the reaction, respectively. Method 2 analyzes the simulation trajectories and determines atom type according to their relative positions.

3 Results and discussion

In this paper, two cases have been designed to compare the differences in reaction, heat transfer and ANP structure between ANP/H₂O and ANP/O₂ system. For the two cases, all configurations are same except that the environmental oxidizer is water for Case 1, and oxygen for Case 2.

3.1 Heat transfer and reaction exotherm

During the reaction, the temporal average temperature of ANP (T_p) were calculated. The temperature profile of Case 1 (ANP/O₂) and ANP/H₂O are plotted in Fig. 2. At $t = 0$ ps, the initial temperature of the ANP is 300 K. As time progresses, T_p increases. Before $t = 70$ ps, temperature of Case 1 is higher than Case 2. But the final temperature of Case 1 is about 2100 K, much lower than Case 2. The contributions of heat transfer and reaction between ANP and oxidizers are analyzed by the kinetic energy variations of ANP and environmental oxidizers. Two methods have been used to calculate the atomic kinetic energies of particle and environment. The energy variation contribution from reaction exotherm (dE_r) and heat transfer (dE_t) are plotted in Fig. 3. As Fig. 3(a) shown, dE from heat transfer is higher than reaction during the first 20 ps. As T_p increase, dE of heat transfer decrease because the difference between T_p and environmental temperature (T_e) reduce. After 60 ps, the dE of heat transfer becomes negative because T_p is higher than T_e and the direction of heat transfer is from particle to the environment. It should be noted that the dE_r of ANP/H₂O reaction is much higher than ANP/O₂. For method 2, the similar tendency is observed except that dE of heat transfer is always positive even though T_p is higher than T_e . When calculating kinetic energy of environment gas molecules, the atoms diffusing into the particle are not taken into consideration. Method 1 seems to perform better because it can capture the heat transfer from particle to environment.

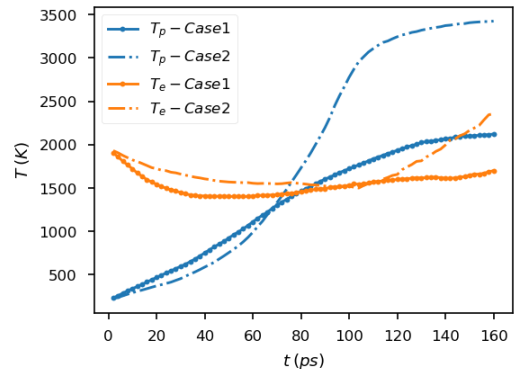


Figure 2: Temporal variations of average particle temperature and environment temperature for Case 1 (ANP/H₂O) and Case 2 (ANP/O₂).

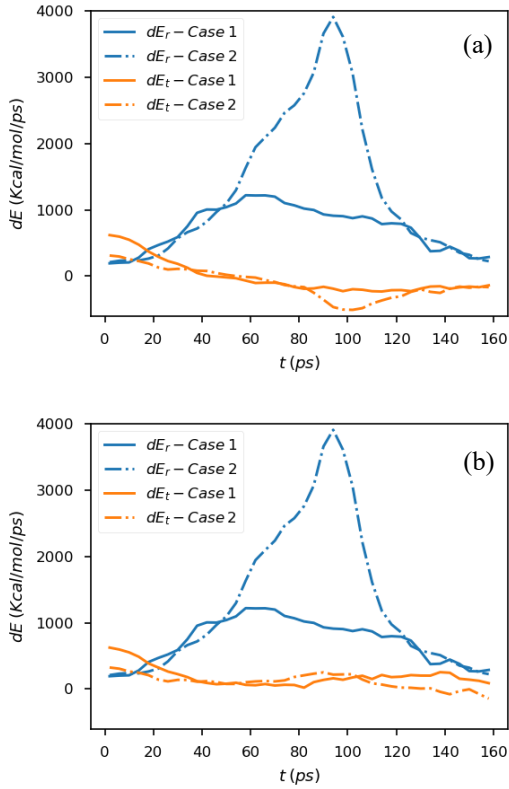


Figure 3: Temporal energy variation contribution from reaction exotherm (dE_r) and heat transfer (dE_t) by Method 1 (a) and Method 2 (b).

3.2 ANP structure

The evolution of ANP structures was then examined. The radial position of core-shell interface and ANP surface are plotted in Fig. 4. The radial position of core-shell and ANP surface are calculated from the average radial position of 30 oxygen atoms in the oxide shell that are nearest to the system center, and 30 Al atoms that are farthest from the center, respectively. In Fig. 4 (a), the cross-section snapshots at different instants are also mapped. The Al core is in blue color while the oxide shell is in red. As the reaction goes on, the radius of Al core shrinks from 25 Å to 0. For Case 1, the curve's gradient is much steeper than Case 2, which indicating the intense reaction between ANP/O₂. As Fig.4 (b) shows, the final radius of Case 1 is larger than Case 2. After the Al cores have been totally reacted, the radius of ANPs are still increase for both two cases. The reaction might not stop after that time. Thereafter, the atomic distribution will be discussed.

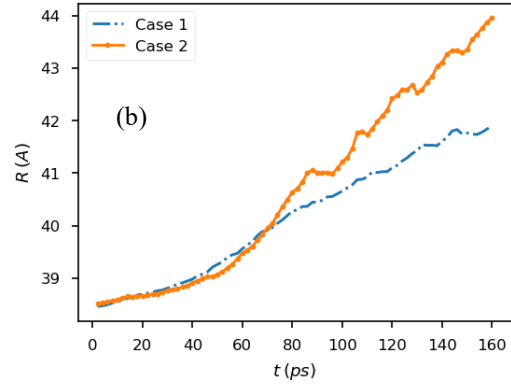
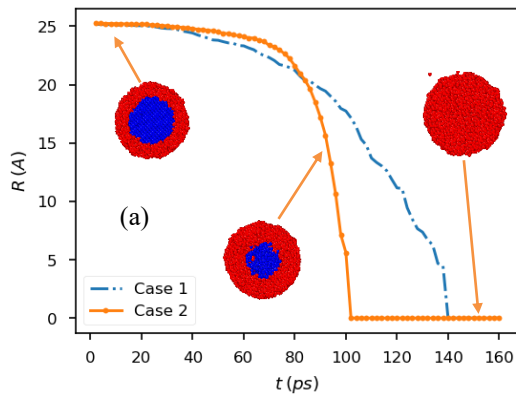


Figure 4: The evolution of core-shell interface (a) and particle radius (b) for two cases.

3.3 Atomic diffusion

To investigate the detail reaction process of two cases, their atomic diffusions are discussed by the atomic distributions of ANP. For Case 1, the final components of ANP are core Al, shell Al, shell O, ambient H and O, respectively. The components of Case 2 are similar except the absence of ambient H atoms. In Fig. 5, the cross-section distributions of different atoms are mapped in contour plots. The computational domain of the central cross section is divided into sub-cells and the numbers of different kinds of atoms in each sub-cell are calculated. To illustrate the atomic diffusion, the initial positions of core-shell interface and ANP surface are indicated by the red and blue curves, respectively. For Case 1, the core Al atoms show crystallized distribution at $t=2$ ps. As T_p increase, the distance between each atom increases and the arrangement of Al atoms become disorder. At $t=80$ ps, the core Al atoms diffuse outward into the oxide shell, which pushes the shell Al atoms outward and results in the expansion of ANP (as Fig.4 (b) shows). The shell O atoms diffuse inward, the atom density in oxide shell decrease and left a vacant lattice site, through which the ambient H and O atoms diffuse into the oxide shell. At $t=160$ ps, the ambient H atoms can diffuse into the central red region, while ambient O atoms fail to reach it, indicating that the diffusivity of ambient H atom is higher than that of ambient O atom. The final ANP is a chemical compound of Al, O and H.

The trend in Case 2 is similar to Case 1. Due to higher T_p , the radius of core Al at $t=80$ ps is larger than Case 1 (as Fig. 4 (b) shows). It can be speculated that as the temperature increase, the Al core will rapidly expand to break the oxide shell. For Case 1, it's not easy for shell Al and ambient O atoms to diffuse into the initial core region (the red circle). While for Case 2 at $t=160$ ps, quite a number of shell Al and ambient O atoms are observed in the initial core region. The final T_p is about 2100 K for Case 1, while for Case 2, it approaches 3500 K. As the melting temperature of bulk alumina is 2345 K. The oxide in Case 1 might be in solid state the atomic diffusion in it is directional, while for Case 2, the oxide is in liquid state and its atoms are free to move around any direction.

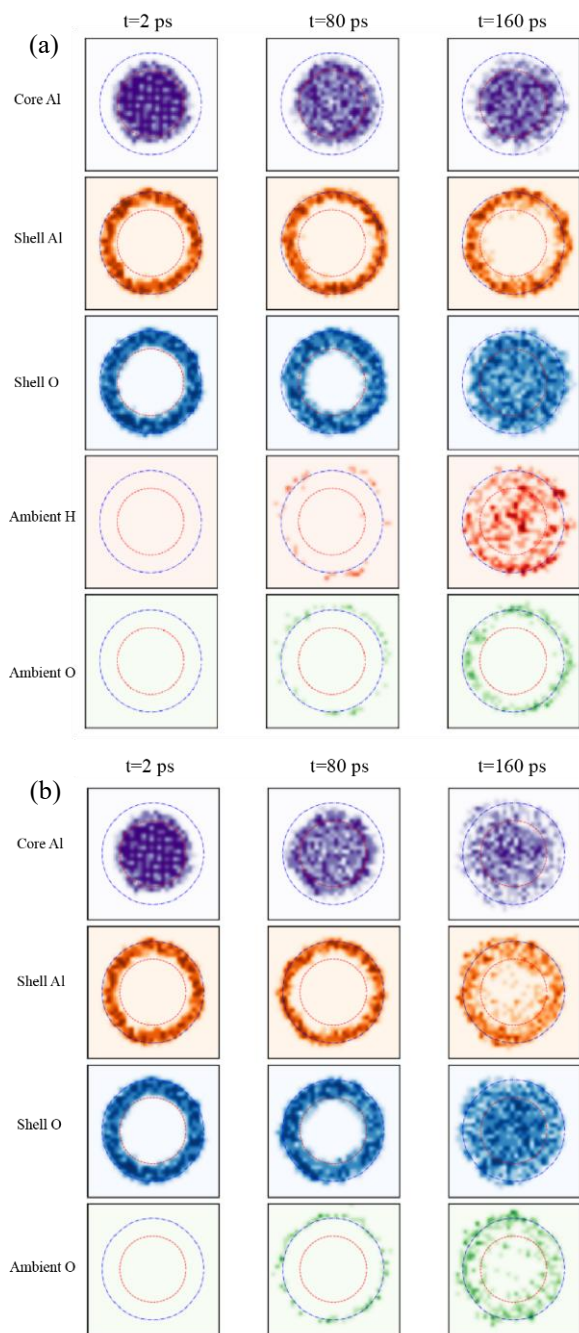


Figure 5: The cross-section distributions of different atoms for Case 1 (a) and Case 2 (b).

4 Conclusions

ReaxFF molecular dynamics simulations have been conducted to investigate aluminum nanoparticle (ANP) oxidation in ANP/O₂ and ANP/H₂O systems at atomic scale. By analyzing the temporal variations of temperature, energy, ANP structure, atomic diffusivities and concentration distributions, the mechanisms of heat transfer and atomic diffusion are elucidated. Main conclusions are summarized as follows:

- (1) At the initial stage of oxidation, the heat transfer between the ANP and environmental oxidizer is dominant. As time goes on, the reaction plays an increasingly significant role.
- (2) The heat transfer efficiency of ANP/H₂O is higher than ANP/O₂, while the reaction exotherm of ANP/H₂O is slower

than ANP/O₂.

(3) The core Al atoms diffuse outward into the oxide shell, which pushes the shell Al atoms outward and results in the expansion of ANP. The shell O atoms diffuse inward and left a vacant lattice site, through which the ambient H and O atoms diffuse into the oxide shell. The diffusivity of ambient H atom is higher than that of ambient O atom in ANP/H₂O system.

5 Acknowledgment

This work was supported by the Equipment Advance Research Field Foundation (Grant No. 61407200201) and National Natural Science Foundation of China (No. 11672314 and 51676016).

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