Ignition and Oxidation of Core-Shell Al/Al₂O₃ Nanoparticles in Oxygen Atmosphere: Insights from Molecular Dynamics Simulation

Qingzhao Chu, Baolu Shi, Lijuan Liao, Kai Hong Luo, Ningfei Wang, and Chenguang Huang

J. Phys. Chem. C, Just Accepted Manuscript • DOI: 10.1021/acs.jpcc.8b09858 • Publication Date (Web): 05 Dec 2018

Downloaded from http://pubs.acs.org on December 16, 2018

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Ignition and Oxidation of Core-Shell Al/Al₂O₃ Nanoparticles in Oxygen Atmosphere: Insights from Molecular Dynamics Simulation

Qingzhao Chu¹, Baolu Shi¹*, Lijuan Liao²*, Kai H Luo³, Ningfei Wang¹, Chenguang Huang²

¹ School of Aerospace Engineering, Beijing Institute of Technology, No.5 ZhongGuanCun South Street, Haidian, Beijing, 100081, CHINA

² Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, No. 15 BeiSihuan West Road, Beijing, 100190, CHINA

³ Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, United Kingdom

Corresponding Authors:
Baolu Shi¹* E-mail: smashingsky@hotmail.com, shibaolu@bit.edu.cn
Tel: +86-10-6891-3623

School of Aerospace Engineering, Beijing Institute of Technology, No.5 ZhongGuanCun South Street, Haidian, Beijing, 100081, CHINA

Lijuan Liao²* Email: liaohuanxin@hotmail.com Tel: +86-10-8254-4291

Key Laboratory for Mechanics in Fluid Solid Coupling Systems, Institute of Mechanics, Chinese Academy of Sciences, No. 15 BeiSihuan West Road, Beijing, 100190, CHINA
Abstract

This study employed the reactive force field molecular dynamics to capture atomic-level heat and mass transfer and reaction processes of an aluminum nanoparticle (ANP) oxidizing in a high temperature and pressure oxygen atmosphere, revealing detailed mechanisms for oxidation of ANPs. Temporal variations of temperature, density, mean square displacement, atom consumption rate and heat release rate of ANP have been systematically examined. In addition, the effects of environment on ANP oxidation were also evaluated. The results show that ANP undergoes four stages of preheating, melting, fast Al core and moderate shell oxidations during the whole oxidation process. The Al core starts to melt from core-shell interface with outward diffusion of core Al atoms into the shell. Intense reaction occurs between shell O and core Al atoms around interface at the end of melting, leading to fast Al core oxidation. After complete oxidation of Al core, the oxide shell continues to react with ambient O atoms. Both the initial environmental temperature and the equivalent pressure significantly influence the preheating. Oppositely, the melting stage seems almost independent any of them. While the fast Al core oxidation presents more sensitivity to the ambient equivalent pressure.
1. Introduction

Owing to excellent energetic properties, such as ultra-high reactivity and high energy density, aluminum nanoparticles (ANPs) have been widely utilized in solid propellants and explosives\textsuperscript{1,2}. Despite wide-ranging existing and future applications, fundamental understanding of the ignition and oxidation mechanisms of ANPs is still lacking owing to extremely complex heat and mass transfer processes involving the Al core, passive alumina shell and environment.

Different oxidation mechanisms have been proposed from extensive studies, which are mainly summarized as three categories. Sundaram et al.\textsuperscript{3,4} pointed out that the oxidation rate of ANPs was controlled by chemical kinetics rather than mass diffusion, and the ANP oxidation scenarios mainly included eruptive oxidation, interfacial diffusion oxidation, and surface diffusion oxidation. For a ductile oxide layer or low heating rates, the ignition of ANPs was attributed to polymorphic transitions of shell and diffusion of aluminum and oxygen atoms across the oxide shell\textsuperscript{5}. An experimental study at low heating rates (<10\textsuperscript{3} K/s) also reported that mass diffusion controlled oxidation kinetics\textsuperscript{6}. As for a rigid oxide layer or fast heating rates, Levitas et al.\textsuperscript{7} proposed a melt-dispersion mechanism, in which mechanical breakdown of the oxide shell prompts dispersion of small Al clusters in the oxidizer, resulting in fast ignition. However, Li et al.\textsuperscript{8} reported that the shell of ANP did not break but just deformed over the oxidation process.

It is seen that so far whether the ANP oxidation rate is controlled by chemical kinetics\textsuperscript{3,4} or mass diffusion\textsuperscript{6} even melt-dispersion\textsuperscript{7} is still uncertain. Due to extremely short reaction time and particle aggregation during ANPs oxidation, it is still difficult to experimentally investigate detailed process of ANP combustion. Recently MD simulation has been employed to provide insights into oxidation mechanism of ANPs. In the study of Wang et al.\textsuperscript{9}, the oxide shell was found to undergo catastrophic failure when the initial core temperature was above 6000 K. Moreover, they also examined the effects of oxide-shell structures on the oxidation of a laser flash heated ANP\textsuperscript{10}. The results showed that ANP covered with an amorphous oxide-shell had much higher reactivity than that with a crystalline one.
Simulations by Henz et al.\textsuperscript{11} demonstrated that the oxidation process was likely to occur by rapid diffusion of aluminum cations driven by an induced electric field through the oxide shell. Zeng and Cheng\textsuperscript{12} performed MD simulations to study the atomic diffusion behaviors of core-shell ANPs during heating process. They argued that the diffusivities of core Al atoms and shell O atoms at the core-shell interfaces decreased by increasing the shell thickness after heating. The inward diffusion of shell O atoms mainly contributed to the initial reaction at core-shell interface.

Most of these models focus on a certain stage, even though they are impressive and enlightening. For example, in refs 9 and 10, the ANPs have been heated to above the melting temperature before the initial oxidation. In refs 11 and 12, ANPs were in vacuum and the effects of surrounding oxygen atoms were ignored. To the best of our knowledge, there are few, if any, systematic studies concerning the whole process of ANP oxidation, while detailed insight into such a process will play a significant role in improving understanding of ANP combustion. The current study adopts a model of preprocessed core-shell ANP oxidizing in hot oxygen atmosphere, which is not only consistent with the real combustion of ANP but also able to capture the atomic dynamics of ignition and oxidation process.

The objective of this work is to capture atomic-level heat and mass transfer and reaction processes of an ANP oxidizing in an oxygen atmosphere; find an effective way that can directly depict the whole process of ANP combustion and quantitatively identify different stages; and quantitatively evaluate the effects of ambient environment on the ANP oxidation. Detailed insight into such a process is helpful in improving control of ANP combustion.

2. Methods

2.1 Computational method

The reactive force field (ReaxFF)\textsuperscript{13} was adopted for the simulation of ANP oxidation. The general expression for total energy used in the ReaxFF is shown in Eq. (1),

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{coulomb}}$$ \hspace{1cm} (1)
in which $E_{\text{bond}}$, $E_{\text{over}}$, $E_{\text{under}}$, $E_{\text{lp}}$, $E_{\text{val}}$, $E_{\text{tor}}$, $E_{\text{vdWaals}}$, and $E_{\text{coulomb}}$ represent bond energy, over-coordination energy penalty, under-coordination stability, lone pair energy, valence angle energy, torsion angle energy, van der Waals energy, and coulomb energy, respectively. 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\textsuperscript{14}. A comprehensive overview of ReaxFF development history can be found in a review literature by Senftle et al.\textsuperscript{15}. 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\textsuperscript{16}. The ReaxFF has been developed for a wide range of chemical systems such as hydrocarbon/oxygen\textsuperscript{17}, silicon/silicon dioxide\textsuperscript{18}, nickel/hydrocarbon interactions\textsuperscript{19}, titanium dioxide/water\textsuperscript{20}, aluminum/hydrocarbon\textsuperscript{21} and aluminum/ethanol interactions\textsuperscript{22}. In ref 15, various ReaxFF applications have also been examined to discuss the breadth of systems that can be modelled with this method. It has been demonstrated that ReaxFF can successfully predict the characteristics of chemically reactive systems. The Al-O ReaxFF parameters used in this paper have been trained and validated by Hong et al.\textsuperscript{13}.

2.2 Simulation details

The simulation mainly included two parts: (1) relaxation under the canonical ensemble (NVT) to form a stable core-shell ANP structure, and (2) heat transfer and reaction between ANP and oxygen under the micro-canonical ensemble (NVE). MD simulation, visualization and data post-processing were conducted by LAMMPS\textsuperscript{23}, OVITO\textsuperscript{24} and Matplotlib\textsuperscript{25}, respectively.

The initial structure of an ANP with an oxide shell was built according to Li’s procedure\textsuperscript{8}. A 6 nm-diameter Al core was cut from face-centered cubic (FCC) Al at 300 K. The amorphous oxide shell was prepared by annealing the alpha-alumina, and then removing the outer and inner concentric parts to obtain an oxide shell of 1 nm thickness. After combining the Al core and the oxide shell together,
the obtained ANP (Fig. 1 (a)) with radius of $R_p = 4$ nm was thermalized under NVT to form a stable core-shell interface. The particle temperature ($T_p$) was controlled at 300 K in NVT ensemble by Nose/Hoover thermostat with a time step ($\Delta t$) of 0.2 fs and a damping parameter of 20 fs. The sensitivities of the time step and the damping parameter have been discussed by the temporal variations of potential energy and $T_p$ in Supporting Information (Fig. S1, $\Delta t = 0.1$ and 0.2 fs; Fig. S3, a damping parameter of 20 fs). A time step as 0.2 fs and a damping parameter as 20 ps (100 times of $\Delta t$) are sufficient to obtain reasonable results.

Figure 1 Snapshots of ANP at $t = 0$ ps (a) and $t = 160$ ps (b) during relaxation in NVT ensemble, initial configuration of ANP surrounded by oxygen molecules (c), and sketch of ANP structure (d). Property distribution within a thin spherical shell (grey shell in (d) with radius of $r$ and thickness of $\Delta r$) was counted.
To obtain a reliable core-shell ANP model, the temporal variation of the particle potential energy was examined as shown in Fig. 2. In this study, the solid lines are the average of three runs while the translucent area indicates the error band. The potential energy changes abruptly during the first 20 ps, which indicates that the initial structure of the ANP is unsteady. At \( t = 120 \) ps, the potential energy varies slightly, and the core-shell interface becomes relatively stable. It should be noted that the curve may continually decrease due to the very slow diffusion between Al and O atoms. The relative error between the potential energy at \( t = 140 \) and 160 ps is less than 1.2%. The time point of \( t = 160 \) ps as the end of relaxation is acceptable. The Al core radius \( (R_c) \) reduced to approximately 2 nm, and the oxide shell thickness \( (\delta) \) increased to 2 nm at the end of relaxation in NVT ensemble. The core-shell interface was determined by the average radial position of 30 O atoms in the oxide shell nearest to the ANP center. Similarly, the average radial position of 30 Al atoms in the oxide shell farthest from the ANP center was adopted as the ANP surface.

Then this configuration of ANP was considered as the beginning of oxidation (Fig. 1(b), \( R_p = 4, R_c = 2 \) and \( \delta = 2 \) nm). The value of \( T_p \) was assigned at room temperature about 300 K initially. Rather than adopting a high temperature Al core in an environment with low temperature in MD simulations reported by literatures, this particle experienced a heating process in an oxygen atmosphere with an initial temperature \( T_a = 2000 \) K and oxygen number \( N_{O_2} = 2700 \) (Fig. 1(c)) in the NVE ensemble with \( \Delta t = 0.2 \) fs for 160 ps. Again, the selection of time step was tested by the temporal variation of the system temperature \( T_{\text{system}} \) in Supporting Information (Fig. S2, \( \Delta t = 0.1 \) and 0.2 fs). It can be convinced that the following calculations with \( \Delta t = 0.2 \) fs are reliable. The simulation was performed in a box of size 160 Å \( \times \) 160 Å \( \times \) 160 Å. The distributions of temperature, density and atom number were counted in a thin spherical shell (with radius of \( r \) and thickness of \( \Delta r \)), as indicated by the grey shell in Fig. 1(d).
Figure 2 Temporal variation of ANP potential energy during relaxation in NVT ensemble.

Cases with different $T_a$ and $N_{O2}$ were assigned in Table 1. Cases 1-3 with the same $N_{O2}$ were designed to evaluate $T_a$ effect on the oxidation and reaction processes of ANP. The equivalent pressure of the environment was represented by the oxygen number in a given volume\cite{13}. Accordingly, the influence of the initial pressure was investigated in cases 1, 4 and 5 at a given $T_a$.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>$T_a$ (K)</th>
<th>$N_{O2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>2700</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>2700</td>
</tr>
<tr>
<td>3</td>
<td>3000</td>
<td>2700</td>
</tr>
<tr>
<td>4</td>
<td>2000</td>
<td>4041</td>
</tr>
<tr>
<td>5</td>
<td>2000</td>
<td>5600</td>
</tr>
</tbody>
</table>

It is important to note that statistical noise is unavoidable in MD simulations, and previous ReaxFF studies indicated that to generate statistically significant results, multiple simulations need to be performed for each of the system\cite{17, 28}. To demonstrate the reproducibility of our results, each case was performed with three samples containing at least 25000 atoms.
3. Results and discussion

This section firstly examines the results of ANP oxidation for Case 1 in Table 1. It focuses on the overall time-evolutions of the ANP temperature, density and mean squared displacement (MSD), diffusion of atoms and variation of oxide structure. The results of five cases are then compared to clarify the effects of initial ambient temperature and equivalent pressure.

3.1 Overall time-evolution of ANP temperature and density

To visualize the reaction process, snapshots of the ANP central cross section are plotted. Thermodynamic properties such as temperature and density in the computational domain of the central cross section were calculated by averaging the properties in all cells. Figure 3 shows representative snapshots of temperature (a) and density (b) in the range of \( t = 0\text{-}160 \) ps. Meanwhile, to make a quantitative analysis, the radial distribution of ANP temperature (a) and density (b) at corresponding time instants were calculated, as plotted in Fig. 4. The radial distribution was plotted by dividing the particle into different spherical shells. For the radial distribution of a property at a distance \( r \) from the centroid of the ANP, atoms in a spherical shell between \( r \) and \( r + \Delta r \) were counted to calculate this property (see Fig. 1(d)). In this paper, \( \Delta r \) was selected as 2 Å.

At \( t = 0 \) ps, the initial temperature of the ANP is 300 K. The density of the Al core is about 2.7 g/cm\(^3\), and that of the oxide shell is nearly 3.5 g/cm\(^3\). The results agree well with the density of solid-state aluminum\(^{29}\) and amorphous alumina\(^{30}\) at 300 K. A low-density region (approximate 2.2 g/cm\(^3\)) is observed near the core-shell interface, which may be caused by the reaction between the Al core and oxide shell. As time progresses, \( T_p \) gradually increases resulting from both heat transfer (between ANP and environment) and heat release from Al/O reaction. At \( t = 60 \) ps, the temperature of the Al core (\( T_c \)) increases to about 700 K, while that of the oxide shell (\( T_s \)) is a bit higher (~ 900 K), indicating the heat transfer process from the outer shell towards the center core. Owing to the small size of the ANP with ultra-low Biot number, the temperature distribution inside the Al core or oxide shell is almost uniform.
Meanwhile, the low-density region propagates toward the center of the Al core.

Figure 3 Representative snapshots of the cross sections of temperature (a) and density (b) distributions of ANP. The dash and dash-dot curves represent the core-shell interface and ANP surface, respectively.

At $t = 80$ ps, $T_p$ rapidly rises to about 1500 K. The distribution of $T_c$ becomes non-uniform, which is caused by local melting and oxidation and will be discussed in Section 3.2. The Al core density reduces to a value lower than 1.7 g/cm$^3$, and the density of oxide shell also slightly decreases. The Al core shrinks, as indicated by the core-shell interface (blue dash lines in Fig. 4), while the particle surface expands outward (dash-dot lines). At $t = 100$ ps, $T_p$ rises to about 2500 K. Near the core-shell interface, the temperature is slightly higher than those at other positions, which is probably attributed to exothermic Al/O reaction at the core-shell interface. The volumes of the Al core and oxide shell vary significantly, indicating the conversion of Al core to oxide shell. And the density distribution illustrates a large gradient around the core-shell interface. From $t = 120$ ps, the Al core is completely
oxidized; the distributions of temperature and density inside the ANP become almost uniform, both of
which increase slightly with $t$. At $t = 160$ ps, the temperature of ANP reaches about 3200 K, and the
density is nearly 3 g/cm$^3$.

Figure 4 Radial distributions of ANP temperature (left) and density (right). The blue, yellow and red
colors represent the Al core, oxide shell and ambient oxygen regions, respectively. The blue dash lines
indicate the positions of core-shell interface, while the dash-dot lines represent the positions of ANP
surface. The arrows show the moving directions of core-shell interface and ANP surface.
3.2 Phase transition and atomic diffusion

Generally, the melting point is defined as the temperature where sharp variations occur in the potential energy, translational-order parameter or radial distribution function profile\textsuperscript{31,32}. In the current study, the inflection point in MSD was adopted to predict the melting\textsuperscript{33}. This point indicates the transition from solid to liquid analogously to phase transition in macroscopy. In the following, the ‘phase transition’ represents the phenomenon similar to solid-to-liquid phase transition. MSD values of the Al core and oxide shell at every step were calculated, which represent the deviation of the atom position with respect to its reference position over time. Here the MSD during 10,000 steps was calculated and defined as MSD\textsubscript{10000}.

In Fig. 5, MSD\textsubscript{10000} and velocity distribution were computed in a cross section with a thickness of 6 Å. Their evolutions were integrated to characterize phase transition and atomic diffusion process. The average velocity of each atom can be determined by counting the displacement of each atom during an interval of 2 ps. The whole physical process is schematically depicted by the first row of Fig. 5, which experiences heat transfer, phase transition and atomic diffusion processes sequentially. Accordingly, four stages, that is, preheating, melting, fast Al core oxidation and moderate shell oxidation are qualitatively defined.

The Al core begins to melt at the core-shell interface from solid phase, as indicated by variation of MSD\textsubscript{10000} (e.g., from \(t = 34\) ps, 2\textsuperscript{nd} row and 1\textsuperscript{st} column to \(t = 68\) ps, 2\textsuperscript{nd} row and 2\textsuperscript{nd} column in Fig. 5). Slight outward velocities indicate that the core Al atoms gradually diffuse into the oxide shell and react with shell O atoms, releasing heat to prompt further melting and oxidation. Outward diffusion velocities of core Al atoms significantly increase as the Al core approaching to the complete melting (e.g., \(t = 88\) ps, 2\textsuperscript{nd} row and 3\textsuperscript{rd} column), resulting in intense core-shell reaction and a rapid shrinking of Al core. This exothermic reaction accelerates the melting of oxide shell (e.g., \(t = 88\) ps, row 3-4 and
3rd column), which further prompts the core-shell reaction and inward diffusion of shell O atoms (e.g., $t = 88$ ps, 4th row and 3rd column). Zeng and Cheng\textsuperscript{12} reported that the reaction initialization of core-shell Al/Al$_2$O$_3$ nanoparticles mainly derived from the inward diffusion of oxygen atoms. We assumed that both outward diffusion of core Al atoms and inward diffusion of shell O atoms contribute to the oxidation. When the Al core has been completely oxidized, the ANP evolves as a nearly homogeneous field (e.g., $t = 124$ ps, row 3-4 and 4th column).

The microstructural evolution of ANP in oxygen environment is illustrated in the bottom row of Fig. 5. During preheating, the ambient O atoms attach to the ANP surface. As the core melts, the core Al atoms obviously deviate from their equilibrated positions and diffuse into the oxide shell. As the core oxidation proceeds, shell O and ambient O atoms diffuse inward serially. The oxidation induced by shell O atoms plays a dominant role, which is different from the previously proposed oxidation mode (Al core react directly with environment O)\textsuperscript{34, 35}. After the Al core has been completely oxidized, ambient O atoms continue diffusing into the shell to improve the oxidation level. Similar to Li’s results\textsuperscript{8}, shell of ANP does not break but just deforms over the oxidation process.

In order to examine the evolution of the ANP structure in more details, variations of the oxide shell size and its components were depicted by the ratio $N_O/N_{Al}$ between O and Al atom number in Fig. 6(a). The shell thickness and $N_O/N_{Al}$ in it hardly ever change until $t = 60$ ps approximately. The core-shell interface approaches to the ANP center in the following 20 ps. This trend remarkably accelerates across 80 ps until the interface diminishes, which indicates extreme outward diffusion of core Al atoms resulting in the decrease of $N_O/N_{Al}$. The diffusion of Al atoms in both core and shell was also examined by the number density, as indicated in Fig. 6(b). A severe decrease of core Al number density around $t = 80 - 100$ ps further confirms the outward diffusion of core Al atoms, as mentioned above. As $t > 100$ ps, the ANP evolves into oxide with homogeneous radial distribution gradually. At the end of
simulation, the radial distributions of $N_O/N_{Al}$ and Al number density with tiny gradients indicate the dynamic equilibrium of atomic diffusion in the liquid phase oxide shell.

Figure 5 Schematic of heat and mass transfer processes (1\textsuperscript{st} row), temporal MSD$_{10000}$ contour and atomic diffusion vectors of core Al (2\textsuperscript{nd} row), shell Al (3\textsuperscript{rd} row) and shell O atoms (4\textsuperscript{th} row), and snapshots of central cross section of ANP (bottom row).
3.3 Definition of four stages

In this section, the four stages as mentioned in Section 3.2 (Fig. 5) were quantitatively defined. The first inflection point (▲) of MSD$_{10000}$ of Al core indicates the transition from preheating to melting stage (Fig. 7(a)). The melting temperature of the core is 827 K on average in our simulations. According to the results of Puri et al.$^{36}$, the melting temperature for bare ANPs with a 5 nm diameter is 790 K, which is close to the current study.

Figure 6 Evolution of ANP structures indicated by atoms distribution contours as well as distribution of O atom number to Al atom number ratio ($N_O/N_{Al}$) in oxide shell (a), and Al atom number density in the whole calculation domain (b). The dash and dash-dot curves are the core-shell interface and ANP surface, respectively.
Figure 7 Temporal variations of global MSD curves for Al core and oxide shell (a), consumption rates of core Al and surrounding O atoms (b), and derivative of system temperature (c). The preheating, melting, fast Al core oxidation and moderate oxide shell oxidation stages are indicated by different greyscales.

The overall time-evolutions of the core Al and ambient O atoms’ consumption rates ($dN_{\text{atom}}/dt$, Fig. 7(b)), system temperature derivative ($dT_{\text{system}}/dt$, Fig. 7(c)) were also examined. Both of them are relatively low in preheating stage, indicating the weak Al/O reaction. As the Al core melts, $dN_{\text{Al}}/dt$ significantly increases, prompting a rapid increase of $dT_{\text{system}}/dt$. The peak of $dN_{\text{Al}}/dt$ (denoted by ■) is defined as the ignition of ANP in this study. Meanwhile, the Al core completely melts. After ignition,
$dN_{Al}/dt$ is maintained at a high value until complete core oxidation (around $t = 106$ ps). At the same time, both $dN/O/dt$ and $dT_{\text{system}}/dt$ approach to their critical values (▼ and ●). In the moderate shell oxidation stage, both $dN/O/dt$ and $dT_{\text{system}}/dt$ gradually decreases, yielding a slow increase of temperature. Ambient O atoms continue diffusing into and reacting with the shell.

In summary, the ANP combustion process can be quantitatively divided into four stages determined by the dominant characteristic parameters in each stage. Different from other studies$^{8-11}$, the preheating and melting processes are analyzed comprehensively in this study. Furthermore, the oxidation process is divided into the fast oxidation stage of the Al core and the moderate oxidation stage of the oxide shell.

### 3.4 Effects of environmental conditions

In this section, the influences of initial ambient temperature and equivalent pressure on the four stages observed in this study were discussed. Five cases were designed as listed in Table 1. The ambient atoms may obtain higher kinetic energy as $T_a$ increases (Case 2 → Case 1 → Case 3). While with increasing $N_{O2}$ (equivalent to environmental pressure, Case 1 → Case 4 → Case 5), the collision of ambient atoms with ANP atoms enhances.

For all cases, the ANPs were ignited successfully with the similar phenomena as Case 1. The durations for the preheating, melting and fast core oxidation stages were counted and plotted in Fig. 8. The elevation of $T_a$ and $N_{O2}$ accelerates the preheating. However, the durations of melting stages in the designed cases vary slightly, which indicates that the effect of surrounding condition could be ignored. For the fast core oxidation, the duration is strongly affected by the equivalent pressure but not sensitive to the environmental temperature.

The energy (heat) transfer between the ANP and the environment is assumed to be accelerated in the preheating stage, owing to the enhancement of the collision probability as $T_a$ and $N_{O2}$ increase.
The Al core melting proceeds from its outer surface to inner as the melting point front propagates inward, which is mainly governed by the thermal conductivity of the Al core at a given size, independent of $T_a$ and $N_{O2}$. For the fast core oxidation, the duration is strongly affected by $N_{O2}$ but not sensitive to $T_a$. Since at this stage, the temperature of the ANP is above 2500 K. The key factor of the fast Al core oxidation is atomic diffusion inside the oxide shell. The elevation of $N_{O2}$ increases the oxygen atom concentrations around the ANP surface, which can accelerate the inward diffusion of oxygen atoms and interfacial reaction.

Figure 8 Durations of different stages under various $T_a$ (left, with a constant $N_{O2} = 2700$) and equivalent pressures (right, with a constant $T_a = 2000$ K).

4. Conclusions

The ReaxFF molecular dynamics has been employed to successfully capture the heat and mass transfer and reaction processes for aluminum nanoparticle (ANP) oxidation in a high temperature and pressure oxygen atmosphere. By examining the phase transition and atomic diffusion processes, atomistic oxidation mechanisms of the ANP are elucidated. Main conclusions are summarized as
follows:

(1) Oxidation of ANP experiences four stages as preheating, melting, fast Al core oxidation and moderate oxide shell oxidation sequentially.

(2) The Al core melting initiates at the core-shell interface, resulting in outward diffusion of core Al atoms. Reaction at the interfacial zone triggers ignition at the end of core melting, which further accelerates Al core oxidation. After complete oxidation of Al core, ambient O atoms continue reacting with the oxide shell.

(3) The outward diffusion of core Al atoms dominates in melting stage, while the inward diffusion of shell O enhances significantly in fast Al core oxidation stage.

(4) Higher initial ambient temperature and equivalent pressure shorten the preheating duration. The melting stage seems irrelevant to them. The equivalent pressure plays a significant role in the fast Al core oxidation stage positively.

The atomistic-level oxidation and reaction mechanisms provide an insight into physical understanding of ANP burning. This study also introduces an analysis and characterization method for size-effect examination in future, which is a key point in the fine controlling of energy release of ANP.

Supporting Information

The sensitivities of the time step and the damping parameter (Figure S1-3); the complete author list for ref 15 (at the end of Fig. S3); the evolution of the ANP cross section (Video).

Author information

Corresponding authors:

Baolu Shi (smashingsky@hotmail.com, shibaolu@bit.edu.cn) ORCID: 0000-0002-8638-4679

Lijuan Liao (liaohuanxin@hotmail.com) ORCID: 0000-0003-1753-6373
Acknowledgment

This work was supported by the Equipment Advance Research Field Foundation (Grant No. 61407200201) and National Natural Science Foundation of China (Grant No. 11672314 and No. 51676016). The computations were supported by the Computing Facility, Institute of Mechanics, Chinese Academy of Sciences, and Tianhe-2 National Supercomputer Center in Guangzhou. KHL’s work was supported by the UK Engineering and Physical Sciences Research Council under the projects “UK Consortium on Mesoscale Engineering Sciences (UKCOMES)” (Grant Nos. EP/L00030X/1 and EP/R029598/1).

References


Measurements of Aluminum Nanoparticle Oxidation with Single Particle Mass Spectrometry.  


(34) Zhang, S.; Dreizin, E. L. Reaction Interface for Heterogeneous Oxidation of Aluminum Powders. 


(35) Nie, H.; Zhang, S.; Schoenitz, M.; Dreizin, E. L. Reaction Interface between Aluminum and 


(a) Temperature (K)

(b) Density (g/cm³)
Oxide shell
Al core
Atomic diffusion
O
Al
O
O
Atomic diffusion
Phase transition
Heat transfer
106 ps
160 ps
60 ps
80 ps
124 ps
1 Å/ps
Core Al
34 ps
68 ps
88 ps
Shell Al
Shell O
Core-shell interface
ANP surface
Oxygen atom in oxide
Oxygen atom in environment
Preheating
Melting
Fast Al core oxidation
Moderate oxide shell oxidation
0.5
1.5
2.5
MSD$_{10000}$
Al atom in core
Oxide shell
Oxygen atom in core
Al atom in oxide
$N_2O_2 = 2700$

$T_a = 2000 \text{ K}$
Atomic diffusion

O Al

Phase transition

Heat transfer

Preheating Melting Al core oxidation Oxide shell oxidation

Al in core

Al in shell

O in shell

O in environment

Atomic diffusion

ACS Paragon Plus Environment