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Collective oxidation behavior of aluminum nanoparticle aggregate

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Aggregates of aluminum nanoparticles are good solid fuel due to high flame propagation rates. Multi-million atom molecular dynamics simulations reveal the mechanism underlying higher reaction rate in a chain of aluminum nanoparticles as compared to an isolated nanoparticle. This is due to the penetration of hot atoms from reacting nanoparticles to an adjacent, unreacted nanoparticle, which brings in external heat and initiates exothermic oxidation reactions. The calculated speed of penetration is 54 m/s, which is within the range of experimentally measured flame propagation rates. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809600]

Aluminum nanoparticles (AlNPs) are widely used in energetic applications such as explosives, rocket propulsions, and other pyrotechniques due their high energy release rate as compared to micron-sized particles. Although there have been many experimental studies on AlNPs focusing on combustion mechanism, energy release rates, and size effects, atomic level understanding of the oxidation behavior is difficult due to small spatio-temporal scale. It has been proposed that while AlNPs oxidize via diffusion through growing oxide shell during slow heating, they undergo drastically different mechanism during fast heating. Under this mechanism, called melt dispersion mechanism, the aluminum core melts resulting in spallation of alumina shell and subsequent ejection of aluminum clusters out of the AlNP. However, this mechanism considers AlNPs as isolated entities and does not describe the overall effect on the entire aggregate. Though experimental images show that the nanoparticles are very closely placed, it remains unexplained how the coupling between proximate AlNPs affects the burning behavior.

With the advent of computing techniques and ever increasing computing resources, researchers have used numerical methods such as molecular dynamics (MD) simulations to gain insight into properties like heat transfer, flow behavior, and size effects in nanoparticles. So far, most of the numerical studies have involved only a few thousand atoms. To study such systems, more comprehensively, large-scale simulations involving millions of atoms are required. In our previous studies, we have used multi-million atom MD simulations to understand the mechanism behind the combustion of single AlNP when subjected to different heating methods. In this work, we extend these methods to study the heat and mass transfer when two hot AlNPs are placed in close proximity of an identical but cold AlNP, in order to gain insight into the mode and mechanism behind the flame propagation in densely packed nanoparticles.

We simulate a linear chain of three AlNPs, where each AlNP consists of an aluminum core of 400 Å diameter covered with a 30 Å amorphous alumina (Al2O3) shell. The alumina shell was cut out from bulk alumina prepared by melt-quench procedure. These three AlNPs are placed 5 Å apart in a line. This system is then placed in an oxygen environment. The size of the MD box is 1938.4 x 969.2 x 969.2 Å3. Each AlNP contains 1973 159 atoms in the Al-core, 856 475 Al atoms and 1 284 281 O atoms in the alumina shell. The surrounding oxygen has 1 888 193 atoms, and the entire system has 14.23 million atoms. In our parallel MD simulations, this system is distributed among 512 processors. The outer AlNPs (left and right) are heated from an initial temperature of 500 K to 1400 K at an average heating rate of 25 K/ps using cycles of velocity scaling for 0.1 ps followed by thermalization for 1 ps, while the central AlNP and the background oxygen are kept at 500 K. After heating, the system is left to react in microcanonical ensemble for 1 ns. A detailed description of the interatomic potential used in this simulation and its validation can be found in Ref. 22. The equations of motion are integrated using velocity-Verlet algorithm with a timestep of 1 fs.

In Figure 1, we show snapshots of the atomic configuration during the simulation. Initially, the oxidation reactions are localized at the core-shell interface in the outer AlNPs and at the fused zones of contact in the central AlNP (Figure 1(a)). These reactions, being exothermic in nature, cause the temperature of the outer AlNP to increase. The shells of the outer AlNPs expand into the core, causing the AlNPs to deform (Figure 1(b)). Atoms from the shell of the outer AlNPs reach their respective centers by 600 ps. The outer AlNPs penetrate into the central AlNP after the melting of the alumina shell (Figure 1(c)), while pushing the shell atoms of the central AlNP into its core. Penetration into the central AlNP begins through the respective zones of contact between the outer and the central AlNPs. This heat and mass transfer from the outer AlNPs increase the number of oxidation reactions inside the central AlNP, while also bringing in external heat. Both these factors cause the temperature of the central AlNP to increase. By 1 ns, all the three AlNPs have fused together to form a single ellipsoidal aggregate (Figure 1(d)).

To understand the flow of heat from the outer AlNPs to the central AlNP and the reaction processes in the three AlNPs, the system is divided into thin slices along the chain, and the temperature distribution is plotted (Figure 2). The initial temperature difference between the outer and central
AlNP can be clearly seen from the curve at 0 ps as a result of preheating of the two outer AlNPs. From 0 to 400 ps, the outer AlNPs gain heat at a much faster rate than the central AlNP, due to the oxidation reactions inside the outer AlNPs initiated by their high initial temperatures. After 600 ps, the central AlNP gains heat at a faster rate than the outer AlNPs. By 1 ns, all the three AlNPs have reached an average temperature of $5500 \, \text{K}$.

We have calculated the rate of increase in the temperature of the AlNPs with respect to time ($\frac{dT}{dt}$), in order to have a deeper understanding of the oxidation process. All three AlNPs show three stages of oxidation, denoted by I, II, and III, in Fig. 3, but the reaction dynamics in the central AlNP is different from the outer AlNPs. The same three-stage reaction was observed in our previous MD simulation of the oxidation of a single AlNP. During stage I in the outer AlNPs, $\frac{dT}{dt}$ decreases as the reactions are localized at the core-shell interface (see supplementary Figure S1 (Ref. 32)). Stage II begins when the alumina shell melts at temperature 2300 K (see supplementary Figure S2), at which point $\frac{dT}{dt}$ begins to increase (Figure 3(a)). The outer AlNPs deform and expand during stage II (see supplementary Figure S3). The onset of stage III in the outer AlNPs is marked by sharp decline in the heating rate, which coincides with ejections of aluminum atoms from the corresponding shells. Although in both outer and central AlNPs, stage I of the reaction occurs in the initial 100 ps, the rate of reaction in the central AlNP is much slower than in the outer AlNPs. When alumina shells in the outer AlNPs melt, they begin to heat the shell of
the central AlNP through the zones of contact. Also, the expansion of the outer AlNPs causes more oxidation reactions in the zones of contact. This increases the heating rate in the central AlNP, thus initiating stage II (Figure 3(b)). Once in stage II, the central AlNP gains heat at a much faster rate than the outer AlNPs. Stage II has a greater time-span in central AlNP than in outer AlNPs with a higher peak in heating rate. To identify the localized regions of reactions, the surface of the central AlNP was divided into small zones, each having 5° as azimuthal and inclination angles (spherical coordinates). The number of atoms in the central AlNP, which have reacted and formed fragments, is calculated for each part over time. When we look at such atoms inside the right circular cone around the y-axis with origin at the center of the central AlNP and aperture = 20°, we find a 19% increase in the first 50 ps, 33% by 100 ps, and 53% by 200 ps. Comparing this with an equivalent right circular cone around the x-axis, we notice a 21% increase in the first 50 ps, 43% by 100 ps, and 77% by 200 ps. This indicates that there are more reactions in the zones of contact as compared to the rest of the core-shell interface in the central AlNP. During stage II, atoms from the outer AlNPs penetrate into the central AlNP through the fused zones of contact and push the shell atoms of the central AlNP into the core at the same time. As a result, more oxidation reactions take place inside the central AlNP in the same amount of time. Stage III in the central AlNP begins at ~600 ps when we observe a decline in the heating rate. It coincides with the beginning of ejection of atoms from the shell of the central AlNP, followed by ejection from its core. The reactions in the outer AlNPs cause them to deform and expand, initiating oxidation reactions inside the central AlNP. The penetration of outer AlNPs into the central AlNP also increases the number of oxidation reactions inside the central AlNP. This, combined with the direct heat transfer from the molten shell of the outer AlNPs, accounts for the heat gained by the central AlNP.

After penetrating, atoms from the outer AlNPs and the shell of central AlNP form Al-rich oxide clusters inside the central AlNP. The number of such clusters is plotted against the distance from the center of the central AlNP in Figure 4(a). As one can see, there is much less penetration into the central AlNP in the first 200 ps. After 400 ps, the clusters formed by the outer atoms are at a minimum distance of 180 Å from the center of the central AlNP, which is still close to the alumina shell. By 600 ps, the outer atoms have penetrated half the radius of the central AlNP and by 1 ns, the outer atoms can be seen to be present at the core.

Figure 4(b) shows the position of different penetration fronts, constituted by the atoms of different origins (outer or central AlNP) and different species (aluminum and oxygen atoms from core or shell). It can be clearly seen that while penetrating into the central AlNP, the different species in the outer AlNPs maintain their relative positions. In other words, atoms from the shell of the central AlNP lead the penetration front, followed by the atoms from the shell of outer AlNPs and finally by the atoms from the core of the outer AlNPs. This indicates that even though the outer AlNPs are penetrating into the central AlNP, they do not break their core-shell structure. The melt-dispersion mechanism16 assumes spallation of the alumina shell, resulting in ejection of clusters from the aluminum core. Our simulation results differ from the melt-dispersion mechanism in two aspects: (1) ejections from the core is preceded by the ejections from the shell; and (2) the core-shell structure is maintained during penetration.

We also calculate the reaction heat generated within the central AlNP (Figure 4(c)) as $E_{\text{rxn}} = KE_{\text{increase}} - KE_{\text{new}} + KE_{\text{out}}$, where $KE_{\text{increase}}$ is the increase in kinetic energy of the central AlNP, $KE_{\text{new}}$ is the kinetic energy of the atoms entering the central AlNP at that instant, and $KE_{\text{out}}$ is the kinetic energy of the atoms exiting the central AlNP at that instant. Between 400 and 600 ps, we see a higher rate of reaction, which is consistent with the observation that during the first 400 ps, no oxide clusters are found within a distance.
of 180 Å from the center of the central AlNP but by 600 ps, such clusters could be found at a distance as close as 80 Å from the center.

The depth of penetration of the outer AlNPs inside the central AlNP is obtained by measuring the average position of the tip of the oxidation front inside the central AlNP at different times during the simulation, and subtracting it from the initial position (Figure 5(a)). The oxidation front is convex in shape (Figure 5(b)) with the tip moving towards the center of the central AlNP. The speed of the oxidation front is estimated to be 54 m/s. Pantoya and Granier\(^7\) have reported a wide range of combustion velocities depending on the size and density of the aluminum nanoparticles. They have found that the combustion velocity in aluminum nanoparticles increase from 1 m/s to 1000 m/s when the reaction pathways shift from solid oxidizer to ambient oxygen gas. While our result cannot directly be compared to these results, it may correspond to the case of high-density aluminum nanoparticles reacting with ambient oxygen.

In summary, we have performed molecular dynamics simulations on a multimillion-atom system of three spherical AlNPs with aluminum core and amorphous alumina shell to study the heat and mass transfer from outer AlNPs to the central AlNP. It was found that once the shells of outer AlNPs melt, they start penetrating into their respective cores, resulting in expansion and deformation of the outer AlNPs. This is followed by penetration of outer atoms into the central AlNP. Before penetration starts, the shell of the central AlNP gains heat due to increased oxidation reactions near the zones of contact when the shell of the central AlNP is weakened due to pressure exerted by the expanding outer AlNPs. The penetration front consists of atoms from the shell of the central AlNP, followed by atoms from the shell of the outer AlNPs and atoms from the core of the outer AlNPs, in that order. The speed of penetration is in conformity with observed combustion velocities in aluminum nanoparticles due to reactions with ambient oxygen. In addition to heating the central AlNP, the hot atoms from the outer AlNPs initiate exothermic oxidation reactions inside the central AlNP, leading to further heating within the central AlNP. It is evident that oxidizing AlNPs can have a considerable effect on the mode and mechanism of the oxidation of a neighboring AlNP. In addition to bringing in external heat via convection, an already reacting AlNP can initiate oxidation reactions inside an adjacent, cold AlNP to a level of self-sustenance.

The combination of these effects results in the cold AlNP oxidizing at a faster rate than an isolated AlNP. Thus, proximity effect should be given appropriate consideration while developing any theoretical model to explain the mechanism behind oxidation of AlNP aggregates.

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\(^28\)R. Clark, Ph.D. dissertation, University of Southern California, 2010.


\(^32\)See supplementary material at http://dx.doi.org/10.1063/1.4809600 for results of oxidation of the outer AlNPs.