Molecular Combustion Properties of Nanoscale Aluminum and Its Energetic Composites: A Short Review

Vinay Kumar Patel,* Amit Joshi, Sanjeev Kumar, Anand Singh Rathaur, and Jitendra Kumar Katiyar

ABSTRACT: Remarkable progress has been established in the field of nanoenergetic materials (mixture of nanoscale fuel and oxidizer) since the advent of nanotechnology. Combustion of nanoenergetic materials depends on many key factors like synthesis route, equivalence ratio, morphology of constituents, and arrangements and handling of materials. For tailoring and tuning of the combustion processes of nanoenergetics, sound knowledge of the reaction mechanism is needed; in this review article a schematic study on the reaction mechanism is presented. By employing various routes and strategies in synthesizing and nanoengineering of the fuel or/and oxidizer to realize a significant evolution from normal physical mixing of nanopowders to the formulation of core/shell nanostructures, the nanoenergetic materials achieved the best ever combustion properties in terms of combustion reactivity, initiation time, energy density, etc. Overall, in this article, a critical state-of-the-art review of the existing literatures has been conducted to feature the main developments in the molecular combustion modeling of melting, oxidation, and core–shell reaction/diffusion of nanoaluminum and the molecular modeling of combustion reactivity and ignition sensitivity of nanoenergetic materials.

1. INTRODUCTION

The study of metal oxide nanomaterials as reactive constituents of nanoenergetic materials was started in 1990 at Los Alamos National Laboratory. It was found that nanoscale aluminum fuel (20–50 nm average size) and MoO_3 reacted together a thousand times faster compared to their macroscale counterparts. Also, the enthalpy of reaction was higher than that of conventional explosives such as TNT (trinitro-toluene). Since then, many investigations have been dedicated to the development of metal oxide based nanoenergetic materials to with regard to stoichiometric ratio, packing density, particle size, etc. These classes of energetic materials are mixtures of metal and metal oxides, for example, Al-CuO, Al-WO_3, Al-MoO_3, Al-Bi_2O_3, Al-Co_3O_4, Al-Fe_2O_3, Al-NiO, Al-NiFe_2O_4, Al-Bi_2O_3, etc., which are stable under normal conditions.

After external triggering (joule heating), they reflect high combustion propagation speed, large amounts of energy, and low ignition temperature. Al/NiFe_2O_4 and Al/NiO have the major advantages of remarkably very low ignition temperatures of 300 and 400 °C, respectively. Nanoboron has been demonstrated to enhance the reactivity of nanoaluminum-based energetic materials of Al-CuO when making <50 mol % of the fuel. The key idea for employing nanoscale reagents is that the diffusion path gets shorter which significantly increases the reaction rate.

The current state-of-the-art development in nanoenergetic materials involves the integration of these reactive nano- materials into micro-electro-mechanical systems (MEMSs) to exploit the available onboard energy for high-end civilian, defense, metal forming, biomedical, and space applications. For these types of applications, a precise understanding and control of reaction rates as well as initiation time is needed. The reactivity of nanoenergetic materials changes drastically as compared to their micrometer size counterparts. Thus, the reactive mechanism for nanoenergetic materials cannot be explained by conventional mechanisms. There are several experimental challenges that limits the understanding of fundamental physical laws that control the reaction mechanism of nanoenergetic materials. Furthermore, challenges arise when the fuel (aluminum) readily reacts with the oxygen and creates a shell of 2–5 nm aluminum oxide which further acts as a barrier to this reaction. With these overall challenges and hurdles, it becomes imperative to switch over from the conventional cohesive theory to the molecular theory of reaction mechanism. The experimental investigation of kinetic parameters and time-resolved mechanism are challenging and too complicated particularly for homogeneous and heterogeneous transformations. Complementing the experimental
investigation of the reaction mechanism of the thermite reactions, atomistic simulations can provide a deeper understanding into the energetic properties. Computer simulations especially at the quantum level can give a brighter picture of thermite reactions without any other experimental setup.

In this comprehensive review, an attempt has been made to cover all the research work done on the molecular combustion analysis of nanoaluminum and its nanoenergetic composites. This paper summarizes the successes achieved in computational modeling methods, mostly molecular dynamics simulations in providing mechanistic insight into predicting the effects of various combinations of nanoenergetic materials on their combustion behavior.

2. MOLECULAR THEORIES OF COMBUSTION

The novel properties of nanoenergetic materials have been extensively studied by experiments, yet they can provide direct measures of results but high experimental costs and limited capacity pose great difficulty for further exploration of desired properties. With the advent of increased computing facility in the last few decades, simulations have emerged as very powerful tools to connect the predictions of theoretical models with experimental results. Based on the problem and spatial scale of interest, a large number of material simulation techniques exist from quantum mechanics simulations to continuum simulations.

There have been continuous efforts in computational analysis of organic energetic materials wherein the research works by Politzer et al. are accounted lots of importance in the domain of thermodynamic and kinetic analysis, heat of formation, impact/shock sensitivity analysis, and reaction mechanisms for decomposition and combustion processes at the ab initio and density functional levels.

Molecular dynamics is a simulation technique that provides an insight into the microscopic mechanisms behind the measured properties and predicts the time evolution of a system of interacting particles. Molecular dynamics approaches allow us to illuminate the mechanisms of nonisothermal processes occurring in nanoscale energetic systems, such as Ni/Al nanofoils, like phase transformations and self-propagation reactions. Material property prediction from chemical composition is often crucial for the improvement of products, especially for materials with a complex structure, and has great value at the stage of design synthesis. Molecular level simulations can play a vital role in the study of these materials not only for the computation of their microscopic physical and chemical properties but also for the atomistic mechanisms that determine these properties, thus providing a link between the micro and macro levels. Molecular dynamics (MD) simulation has proven to be an excellent tool in understanding the gas–solid interface reaction mechanism of nonoxide ceramics. In molecular simulations, a limited number of atoms/molecules are selected and initially their positions and velocities are assigned. In the MD method, electron effects are averaged out and time evolution of atomic position and velocities are computed from the Newton equations of motion. Electron related approximations are based on the Born–Oppenheimer theory. The MD time step which is used to describe the atomic motion is long enough for the electrons to achieve their ground state due to the faster speed of the electron in comparison with the nuclei; this is caused by their mass difference. The interatomic potentials (force fields) are established from the first principle or experiment to reproduce the forces to describe interactions among the atoms including the effect of electrons. The reliability of the interatomic potential determines the accuracy of the MD simulations and is furthermore related to the ability to bridge to mesoscale method validity. The system behavior is precisely checked with the evolution of all atoms and the calculation of all forces. The position and velocity of each atom is updated within a finite
time step. The time step is chosen by the fastest motion of the atom in the system, mostly of 10 fs order. Thus, a 1 fs time step is mostly used in MD simulations. Due to restrictions in time step, only a simulation of a few picoseconds to nanoseconds is possible to date and also the size of the simulation is limited to say a few nanometers (100 nm).

Molecular dynamics simulations are quite similar to real experiments. As in a real experiment a sample is prepared and a test is performed with the help of measuring instruments, thereby a statistical average of a desired property is measured. In a similar manner in MD simulations, a model of a system having a finite number of atoms (N) is selected, and thereby, Newton’s equations of motion are integrated by employing numerical methods like the Verlet algorithm (pure Verlet method or leapfrog method) or Gear predictor algorithm until the average properties of the system have very little variation with time. A basic methodology of MD simulation is presented in Figure 1.

2.1. Molecular Theory of Combustion of Nanoaluminum. Nanoaluminum is considered as a potential solid propellant owing to its inherent properties like high combustion enthalpy, good catalytic activity, high reactivity, and fewer environmentally degradable combustion products. Many researchers have focused their research on the study of combustion kinetics of aluminum materials. Although much research is still devoted to the study of the nanoaluminum combustion mechanism, the phenomenon behind this is due to the polymorphic phase change in the oxide layer or the pressure built up on melting of the aluminum core. Recently, molecular dynamic simulations have played a vital role in the study of the thermal properties of nanoaluminum.

2.1.1. Molecular Theory of the Melting of Nanoaluminum. The melting behavior and the temperature at which any particle melts depends on its size. With the increase in the size of a particle, the melting behavior and the melting point approaches that of the bulk. Particles having radii ~10 nm and larger can be analyzed with thermodynamic models, although surface tension effects can cause these melting points to be lower than that of the bulk. MD simulations are reported to determine the melting points of aluminum nanoparticles of 55–1000 atoms using the Streitz–Mintmire ES+ potential through the study of the temperature dependence of the potential energy and Lindemann index. It was observed that the aluminum nanoparticles (less than 850 atoms) exhibited bistability between the solid and liquid phases over temperature ranges below the point of complete melting thus revealing the characteristic of dynamic coexistence melting while at higher temperature only the liquid phase was stable. They developed a very useful correlation of the variation of the melting point of aluminum nanoparticles as a function of the number of atoms (Figure 2a) and a function of effective radii of Al nanoparticles (Figure 2b). The melting points were counted to be the temperature at which there was a sharp rise in the Lindemann index with the “error bars” showing the lower and upper bounds of the bistable region determined from the potential energy studies. It was revealed that the melting points of larger nanoparticle generally increase monotonically with size. For nanoparticles with up to ~200 atoms, the melting point did not vary monotonically and showed some magic number effects. The magic number nanoparticles are denoted in Figure 2 with white square symbols. Alavi et al. observed a shift of the range of bistability toward higher temperatures as the size of the nanoparticle increases, and the bistable range became shorter for larger nanoparticles. For large nanoparticles (from 923 atoms), the bistability was no longer present, and the melting behavior became similar to the bulk melting. The largest nanoparticle in their MD simulations with 1000 atoms had not approached the bulk limit in terms of its melting behavior.

In a comparative study for force fields, Puri et al. performed the MD simulation using isobaric–isoenthalpic (NPH) ensembles to model the melting behavior of nanoaluminum with varying aluminum particle size from 2–9 nm using five different potentials by considering both bulk and particle melting. They found a monotonic increment in the melting temperature of a nanoparticle with increasing the size with the result of 473 K at 2 nm to a bulk value of 937 K at approximately 8 nm. For nanoparticle sizes less than 3 nm, the solid and liquid phases were observed to coexist. The researcher employed five force fields of LJ, Glue, EAM, Streitz–Mintmire, and Sutton–Chen potentials and, through thermodynamic parameters like the Lindemann index, translational order, radial distribution, etc., studied the melting process behavior. Out of these five potentials only the many-body Glue and Streitz–Mintmire potentials had accurately predicted the bulk melting points of 1244 and 1146 K, respectively (which are greater than the thermodynamic melting point by about 18%). As shown in Figure 3, the melting behavior shows a fluctuation in temperature, with, out of four potentials, only Glue and Streitz–Mintmire potential energies predicting the melting point close to experimental values. The experimental melting temperature of bulk aluminum metal is 933.5 K. The thermodynamic melting point is approximately 0.75–0.85 times its structural (simulated) counterpart. After applying this factor, they simulated the thermodynamic melting point to a value close to 940 K for bulk aluminum.

Puri and Yang studied the effect of internal void defects on the melting of bulk and nanoparticulate aluminum using NPH ensemble based MD simulation. For the same size range of 2–9 nm, they postulated a variety of shapes and sizes and compared the results with perfect crystals. They observed that the presence of voids did not impact the melting properties owing to the dominance of nucleation at the surface, unless the void size surpassed a critical value beyond which lattice collapse occurred. For 5.5 and 8.5 nm particles, the critical void
sized were simulated to be 1 and 5 nm³, respectively. They obtained the ratio of the structural to thermodynamic melting points as 1.32 independent of shape and size of voids with the structural melting temperature of bulk melting of nanoaluminum to 1244 K.

In another MD simulation, Puri and Yang⁵g studied the effect of the crystalline and amorphous oxide layer coating of range 1−2.5 nm on the thermomechanical behavior of nanoaluminum particles (size range 5−10 nm) during the melting process employing the Streitz−Mintmire potential, along with microcanonical (NVE) and NPH ensembles. They observed that the oxide layer melted at about 1100 K, substantially lower than the bulk alumina temperature of 2327 K; however, the melting temperature of the aluminum core was substantially lower than its bulk value of 940 K. The results were compared to the pure 5 nm alumina nanoparticle, for which the melting was witnessed at 1284 K.⁶g Li et al.⁶b observed different melting behavior of the Al₁₉₆ cluster when simulated by MD methods combined with annealing and quenching techniques. The Li group’s simulation utilized Gupta semiempirical potential and found a linear relationship for the cluster size and melting point. As the cluster size increased, the melting point also increased.

2.1.2. Molecular Theory of the Oxidation of Nanoaluminum. Campbell et al.⁶a reported the first parallel MD simulation of the oxidation of aluminum nanoparticles of diameter 20 nm based on dynamic charge transfer among atoms. Large pressure variations were investigated during the oxide growth which led to rapid diffusion of atoms in the oxide. The significant charge transfer gave rise to large negative pressure in the oxide which was dominant to the positive pressure due to steric forces. The structural analysis demonstrated the formation of a 4 nm thick amorphous oxide layer consisting of mixed octahedral, Al(O₁/₆)₆, and tetrahedral, Al(O 1/₄)₄, configurations during 466 ps of simulation time which was in excellent agreement with experimental results on aluminum nanoclusters. Further, Campbell et al.⁶b reported similar findings during the MD study of the dynamics of oxidation of aluminum nanoclusters (diameter 20 nm) considering the effect of charge transfer between Al and O based on the electronegativity equalization principle. The local stresses in the oxide scale caused the rapid diffusion of aluminum and oxygen atoms. A significant charge transfer was revealed in the reactive region (oxide scale) in the microcanonical and canonical simulation leading to rise of large negative pressure in the oxide.

Clark et al.⁶c performed the multimillion-atom reactive molecular dynamics simulation using the embedded atom method (EAM) potential along with a bond order coupling scheme to study the mechanisms that govern the heat-initiated oxidation in aluminum nanoparticles. They observed the occurrence of oxidation in three systematic stages: (i) confined burning, (ii) onset of deformation, and (iii) onset of small cluster ejections. In the first stage, a strong local heating and an increased migration of oxygen from the shell into the core proceeded. After approaching the local temperature above the melting point alumina shell (T = 2330 K), the melting of the alumina shell initiated causing the second stage of deformation of the overall particle through producing increased heat. Further in the third stage at above 2800−3000 K, small aluminum clusters were ejected outwardly from the shell.⁶c Henz et al.⁶d simulated the mechnochemical behavior of oxide coated nAl (core diameter 5−8 nm, thick oxide shell 1−2 nm) using classical MD and demonstrated that an induced electric field across the oxide layers caused by heating of the particle empowered the diffusion of the aluminum from the center of the particle. The induced electric field accounted for ~90% of the initial mass flux of Al ions through the oxide shell. Their results showed good agreement with published theoretical and experimental literatures.⁶d

Hong and Duin⁶e conducted the ReaxFF-MD simulations to study the oxidation of aluminum nanoparticles (nAl) at different temperatures and oxygen density to illuminate the mechanism of the oxidation kinetics of the nAl and found the oxidation states in the oxide layer. Their simulation revealed the oxidation mechanism as (i) creation of hot-spots and high temperature regions through the adsorption and dissociation of oxygen molecules over the surface of the nAl, (ii) creation of void spaces due to these hot-spots and high temperatures, and (iii) minimization of the reaction barrier for oxygen diffusion by the created void spaces (by up to 92%) promoting accelerated oxygen diffusion. The high pressure of the oxygen enhanced the possible number of void spaces at the outer surfaces of the nAl, whereas the high temperature increased the possible number of void spaces throughout the bulk of the nAl. The density of the oxide layer was influenced by the combined effects of the system temperature and oxygen pressure. These ReaxFF data conformed to a good agreement with available experimental results on aluminum oxidation kinetics.⁶e

2.1.3. Molecular Core−Shell Theory of Nanoaluminum. Many of these studies were dedicated to learning the oxidation mechanism of nanoaluminum. In a multimillion MD study, Wang et al.⁷a found that the oxide shell structure also played a role in reactivity and the amorphous oxide shell had higher reactivity as compared to the crystalline oxide shell. They observed a thermal-to-mechanochemical transition of oxidation mechanism when the initial core temperature crossed 6000 K. The higher initial temperature of the core caused catastrophic failure of the shell, which led to faster and more complete oxidation of core Al, resulting in faster energy release rates. The experimental results of Zachariah’s group also confirmed the creation of hollow nAl after oxidation at elevated temperatures.⁷b

Also in another multimillion MD simulation study, Shekhar et al.⁷c revealed a higher reaction rate in a chain of aluminum nanoclusters than when the aluminum nanoparticles were
isolated. It is manifested that the oxidizing nAl had a considerable effect on the mode and mechanism of the oxidation of a neighboring nAl by bringing an additional convection heat transfer to the neighboring nAl. Thus, already, nAl could initiate the oxidation reactions inside a neighboring cold nAl to a level of self-sustenance resulting in a greater reaction rate in nAl aggregates than the isolated one. In another MD simulation integrated with ReaxFF reactive force field of the Al/Al2O3 core–shell, Zeng et al.24 concluded that the diffusivities of Al and O atoms at the core–shell interface were irrelevant to shell thickness during the heating process which decreased as the shell thickness increased after the heating process. They demonstrated an inward diffusion of shell oxygen atoms which had a major contribution to the initial core–shell interfacial reactions. They observed the presence of a significant void space during the melting of the alumina shell, which agreed well with the experimental results. The alumina shell of 1 nm thickness melted at 1153 K, and the melting point increased with the increment of the shell thickness.25

A study conducted by Chu et al.7e simulated the nano-aluminum core–shell at a high temperature and pressure oxygen atmosphere and divided the oxidation process into four stages, viz., preheating, melting, fast aluminum oxidation, and oxide shell oxidation. In this study they found that the core aluminum diffused outwardly at the core–shell interface which caused a violent reaction. Also they studied the variation in burning time with changes in ambient temperature and pressure. Figure 4 describes the variations in durations of the preheating, melting, and fast core oxidation stages with changes in ambient temperature at a constant oxygen number (N02) of 2700 (left) and with the change in oxygen numbers (equivalent pressure) at constant ambient temperature (Tc) and 2700 K (right). From Figure 4, it was revealed that the elevation in ambient temperature and oxygen atmosphere pressure accelerated the preheating, but it slightly affected the melting process, which indicated that the surrounding conditions could be ignored. For the fast core oxidation, the duration was insensitive to the environmental temperature but was strongly affected by the equivalent pressure. Table 1 shows the various simulation and modeling methodologies followed by researchers to study the melting behavior of aluminum.

2.2. Molecular Theory of Nanoenergetic Reaction. Nanothermites are a class of energetic materials containing both fuel (like nanoaluminum) and oxidizer (like CuO, Fe3O4, MoO3, NiO) which on burning goes into a rapid redox reaction.8a In order to achieve a controlled reaction, it is important to understand the fast thermite reaction in detail. Molecular dynamics simulation is an effective tool for the investigation of the physical and chemical properties and kinetics of the energetic redox reaction. It can help to visualize the detailed initiation decomposition steps and postreaction decomposition processes. For getting a deep insight into the thermite redox reaction on an atomic scale, a considerable number of molecular dynamics simulations have been performed. Among many reactive nanocomposites, the Al/CuO bilayer nanofoils exhibit a good model system to study reactive interfaces wherein a composition of a nanolayer of Al (fuel) and a nanolayer of CuO (oxidizer) is deposited to develop a multilayered thin film of Al/CuO by magnetron sputtering formulating good control over thickness and purity and producing a maximum theoretical heat of reaction.8b

Tomar and Zhou9a,b developed an interatomic potential that described the interatomic interactions in the Fe, Al, Al2O3, and Fe3O4 system and calculated shock wave propagation of fcc Al and α-Fe2O3. Shimojo et al.10a–e studied the reaction kinetics of Al-Fe2O3 using first principle ab initio calculations. Here these scientists proposed a concerted Al−oxygen flip mechanism at the interface which improves the reaction rate and mass diffusion. Ming et al.11 studied the bond formation and redox reaction over a time scale for the Al/Fe2O3 interface. All these studies conclude that the thermite reaction is mainly promoted at the interface of the Al/metal oxide. Based on numerous studies, it can be confirmed that the combustion behavior of nanothermites can be greatly enhanced by making proper interfacial contact among the reactants.3a Thus, the current research is based on structural systems in which there is close interfacial contact between the fuel and the oxidizer. The morphology of the reactants plays an important role in controlling the interfacial and contact area. Nanolaminates possess good planar interfacial contact among fuel and oxidizer and currently are a hot topic of research in this field. Lin et al.12 and Zhu et al.13 studied the nanothermite reaction based on ReaxFF force field and concluded that the thermite reaction of these nanolaminates depends on many factors like the proportion of metal (aluminum) and oxide (Fe2O3), initial temperature, heating rate, and initial distance between Al and Fe2O3. The ignition delay as well as reaction time of the thermite reaction can be considerably reduced by increasing the preheating temperature. Lin demonstrated the relationship of ignition delay with heating rate and initial ignition temperature as depicted from Figure 5. With different heating rates (3, 1.5, and 0.15 K/ps), the ignition delay decreases with an increase in the heating rate. By varying the initial ignition temperature (Tini), ignition delay shortens with an increase in Tini. Zhu et al.13 demonstrated as shown in Figure 5 that as the heating rate increases from 0.5 to 3 K/ps the ignition delay widened and also ignition temperature goes down from 1450 to 1200 K which contradict the experimental results. In this study researchers focused on the number of bonds formed by aluminum−oxygen, and the jump in the graph shows the reaction between aluminum and oxygen. From Figures 5 and 6, contradictory results are shown. The possible reasons for such results by Zhu et al. might be due to not taking a Noose−Hover thermostat in an NVT ensemble and the adiabatic NVE microcanonical ensemble into consideration while performing reaction simulation in stage 3. Similar results were obtained by

![Figure 4. Variation in duration with varying initial temperatures and oxygen pressures.](image)
Table 1. Modeling Strategy Followed by Researchers for Melting Behavior of Aluminum

| ref            | modeling                                                                 | morphology and size                      | findings                                                                 |
|----------------|--------------------------------------------------------------------------|------------------------------------------|--------------------------------------------------------------------------|
| Wang et al.    | EAM potential with about 1,018,467 atoms in a 226.419 nm MD box. Core heated to 3000, 6000, and 9000 K, respectively. | 48 nm aluminum, 4 nm alumina           | The higher temperature of the core (9000 K) shows better combustion and higher energy release rates. |
| Alavi et al.   | Streitz–Mintmire variable charge potential and calculation of melting of nanoaluminum particles by the Lindemann index | nanoparticles with varying numbers of atoms from 55 to 1000 atoms | Nanoparticles with less than 850 atoms show bistability in solid and liquid phases while higher atoms show a sharp solid–liquid phase transition. |
| Chu et al.     | ReaxFF force field in LAMMPS software using the NVT canonical ensemble for relaxation and NVE microcanonical ensemble for reaction of aluminum with oxygen. | 6 nm aluminum with 1 nm oxide shell     | Ambient pressure and initial temperature dominates the reaction mechanism. During the melting core aluminum diffuses outwardly while oxygen diffuses inwardly during oxidation. |
| Campbell et al. | Streitz–Mintmire potential with multipole method and multiple time-step algorithm | 325,158 aluminum atom sphere of 200 Armstrong diameter was distributed along with 530,720 oxygen atoms. The density of oxygen was 40 times that of ambient conditions to mimic high temperature and pressure. | Aluminum diffuses 30–40% higher than oxygen in the oxide. Also octahedral Al(O1/6)6 and tetrahedral Al(O1/4)4 formations are there. |
| Campbell et al. | Streitz–Mintmire potential with multipole method and multiple time-step algorithm | 325,158 aluminum atom sphere of 200 Armstrong diameter was distributed along with 530,720 oxygen atoms | During oxidation a large diffusion of atoms in oxide growth facilitate large pressure variations. Diffusion of oxygen in oxide occurred inwardly, and that of aluminum occurred outside. |
| Henz et al.    | ReaxFF force field in general reactive atomistic simulation program (GRASP) in parallel computing environment | 0.1 million atoms of 5.6 to 8 nm diameter aluminum with 1 and 2 nm thick alumina | At very high heating rates the mechanism of oxide diffusivity was due to induced electric field in the oxide shell. |
| Puri et al.    | NPH ensemble and five potentials (LJ, Glue, EAM, Streitz–Mintmire, and Sutton–Chen) | 2–9 nm nanoaluminum particles. | Only Glue and Streitz–Mintmire potentials accurately predict the melting behavior of nanoaluminum with varying particle size. |
| Puri et al.    | Streitz–Mintmire potential with isobaric–isoenthalpic (NPH) and microcanonical (NVE) ensembles, predictor corrector, and Verlet algorithms | 5–10 nm size aluminum with 1–2.5 nm oxide thickness | The oxide layer melts at a much lower point in the range of 986–1159 K and depends on the size of the aluminum oxide layer. |
| Hong et al.    | ReaxFF force field, canonical (NVT) ensemble with Nose/Hoover thermostat in LAMMPS, varying the oxygen density and temperature | 504 Al atoms of (4,3,1) slab and 864 aluminum cluster atoms with 2.8 nm diameter | Pressure and temperature play major roles in the oxidation behavior of aluminum. High temperature causes the formation of suboxides while high pressure is responsible for the formation of suboxides to oxide (Al2O3). |
Zeng et al.\textsuperscript{14} in studying the behavior of Al/NiO; with the increase in ignition temperature, the ignition delay shortens. The modeling strategy used by the author was NVT and Nosé–Hover thermostat while heating the system up to its ignition temperature and performing the thermite reaction in the microcanonical adiabatic (NVE) ensemble.

The interface problem can be best addressed by core–shell structures as they exhibit lower ignition temperature and a direct interface between the two reactive components. Among aluminum based nanothermites Al/CuO possesses high energy density (21 kJ/cm\textsuperscript{3}), and also, these nanothermites offer good compatibility with core/shell deposition. Kwon et al.\textsuperscript{15} studied a detailed interfacial chemistry and its role in redox reaction in Al/CuO nanothermites. Based on experimental studies and first principle ab initio calculations, the researchers found that employing atomic layer deposition (ALD) using trimethylaluminum (TMA) shows better reaction properties as compared to nanothermite formed by physical vapor deposition (PVD). By employing TMA in the system the diffusion process of oxygen from CuO to Al is governed by the interface between CuO and Al (in this case a carbon of the methyl group acts as a ligand) rather than the thickness of the alumina layer. Similar observation was recorded by Lanthony et al.\textsuperscript{16} while employing first principles calculation (DFT) on CuO/Al nanolaminates. The study is based on the early stage adsorption of CuO to the aluminum surface, where copper promotes aluminum–oxygen interaction and also separates the resulting alumina from the aluminum substrate. Cheng et al.\textsuperscript{17} utilizes molecular dynamics simulation to study the thermodynamic properties of the Al/Cu core–shell structure. These researchers utilize embedded atom method (EAM) potential and investigate the melting and cooling behavior of the Al/Cu system with slow and fast cooling rates. Tang et al.\textsuperscript{18} studied the thermite reaction at the Al–CuO interface with varying temperatures. With the increase in temperature, the reduction of copper expands towards the copper rich interface while the oxidation (exothermic) reaction between aluminum and oxygen expands towards the oxygen rich interface. Similar findings were justifi ed by Xiong et al.\textsuperscript{19} while performing ab initio calculations to investigate the reaction kinetics of Al/CuO at high temperatures. In this study as the temperature of the system increases above 2000 K, the atomic configuration of reactants changes at a faster rate. At lower temperatures of 830 and 1000 K, the interface reactions were incomplete.

Experimental studies for the investigation of interface formation are limited with high enough spatial resolution.
On the other hand, with the help of simulation studies one can investigate reaction mechanisms based on hypotheses governed by experimental findings. Nickel oxide has drawn a great deal of attention in the scientific community especially for microinitiator applications because of the gasless thermite reaction of Al/NiO; also they have a low onset temperature and high heat output. Wen et al. synthesized Al/NiO nanocomposites with varying stoichiometric ratios and found a considerable increase in energy release with an increase in NiO ratio; however, this had an intangible effect on onset temperature. By performing ab initio calculation, the authors claim that there is an Al–Ni phase present after the reaction. Fathollahi et al. investigated the reaction mechanism and diffusion rate of oxygen into aluminum in the Al/NiO thermite reaction by employing the ReaxFF force field. In this molecular dynamics study the thermite reaction was initiated at five varying temperatures and the predicted onset temperature for the thermite reaction was close to the experimentally predicted value of 1149 K. Another study done by the same group concluded that at 500 K there is no reaction occurring between Al/NiO. In this work, the authors investigated both experimentally and through molecular dynamics study that the onset temperature of Al/NiO is 1154 K which is in good agreement with the experimentally calculated value of 1166 K. In order to increase interfacial contact area, Al/NiO honeycomb nanostructures have been realized, results of which show good combustion properties such as high reaction energy and temperature, tailored dimensions, and easy integration. Zeng et al. studied the honeycomb Al/NiO nanothermite reaction process through molecular dynamics simulation. By simulation the adiabatic reaction temperature and activation energy were calculated to be 5500 K and 8.43 kJ/mol, respectively, which were far from the experimental values of 3960 K and 2.2 kJ/g.

3. CONCLUDING REMARKS

In order to put energetic nanocomposites into service precise control over the rate of reaction is needed. For this effort, the fundamental knowledge of the combustion behavior must be addressed. In order to get deeper insight into the combustion behavior, many researchers have proposed various mechanism for reaction front behavior of various compositions of these nanocomposites. A detailed review of molecular reaction mechanisms was conducted in this paper. Overall the major focus of today’s researchers in the field of energetic materials has been on enhancing the combustion properties (combustion wave speed, combustion pressure, pressurization rate, energy released, heat of reaction) of nanocomposites by increasing the surface area of constituent metals and metal oxides along with increasing the intimacy between the metal and metal oxide.

By employing computers for simulating the nanoenergetic composites, a better understanding can be achieved regarding the mechanism prevailing during the reaction of fuel and oxidizers. However, the calculations in molecular dynamics so far performed were based on classical and semiclassical approximations of quantum mechanics. Although these calculations are valid, they are not so accurate; now quantum calculations are often computationally extensive and cannot model big systems. Also much work is needed to develop an accurate potential field and modeling technique to mimic the actual conditions. Most simulations are now limited to small size; however in the near future, large systems may be simulated at lesser computational cost.

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#### Notes

The authors declare no competing financial interest.

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