Combustion of Al nanoparticles coated with NC/ethanol/ether molecules by equilibrium molecular dynamics simulations

Xin Jin  
Harbin Engineering University

Lei Wang  
Harbin Engineering University

Pingan Liu (✉ liupingan631@126.com)  
Harbin Engineering University

Penghua Sui  
Harbin Engineering University

Article

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Abstract

Al nano-particle (ANP) have high reactivity, but they are easily inactivated by external oxidants. To improve its surface property, we coat ANPs with nitrocellulose (NC)/ethanol/ether solution. And MD simulation method is used to simulate the coating, ignition and combustion processes of ANPs under three different coating conditions. Our results show that the NC/ethanol/ether formed a dense coating layer on the surface of annealed ANPs and passivated ANPs through physical and chemical adsorption. The coating layer can block the contact between the active Al atoms and O$_2$ molecules at low temperature. In ignition phase, NC/ethanol/ether coating layer can increase the density of O$_2$ molecules around ANPs and the surface temperature of ANPs. At the same time, due to the desorption and diffusion of the coating layer exposed more reaction sites, ANPs have shorter ignition delay and lower ignition temperature. According to the change of atomic displacement, the combustion stage can be divided into three stages. The NC molecules can increase the combustion propagation speed, combustion time and efficiency of ANPs. Such improvement will enable ANPs to obtain better storage performance, combustion performance and play a stronger role in the field of energetic materials.

1. Introduction

Energetic material is a kind of compound or mixture that containing explosive groups or combustibles and oxidants. Under certain external stimuli, it can conduct redox reactions alone and release a large amount of energy (usually accompanied by a large amount of gas and heat). As a typical energetic material, ANPs play an important role in propellants. ANPs have high specific surface area and reactivity due to the defects of bond state, electronic state and atomic coordination on the surface of nanoparticles. Using ANPs can greatly improve the combustion efficiency, the dynamic and static burning rate of high energy condensed system, improve the detonation heat and greatly reduce the activation energy of combustion system. However, those characteristics not only improve the application advantages of ANPs in propellants, but also bring difficulties in storage and processing. The newly prepared ANPs are easily oxidized or even spontaneous combustion in oxidation environment $^{[1, 2]}$.

To improve the surface properties of ANPs, researchers propose a concept of constructing stable envelope structure on particle surface. After cladding, ANPs have a passivation layer on the surface which isolate the contact between the external oxidation environment and the active Al atoms. By changing coating materials, we can get core-shell composite particles with different surface properties. As an important part of solid propellant, NC with high nitrogen content has the characteristics of water resistance, acid and alkali resistance, low cost and long storage life $^{[3]}$. Moreover, the NC fiber bundle will undergo the process of swelling to dissolution in the solvent and the molecular chain is dispersed in the solvent to form a homogeneous sol. Therefore, preparing the stable structure core-shell composite aluminum particles with NC sol is of great significance for the storage of ANPs and its application in propellants $^{[4]}$. 
Most researchers used experimental methods to study NC/ANPs composite particles. Michael R. Zachariah et al. from the University of Maryland carry out a large number of studies on Al-NC composite particles prepared by electrostatic spray method \[5\]. They find the combustion efficiency of Al-NC composite particles prepared by electrostatic spray method is basically equivalent to that of non-agglomerated nano-aluminum powder in combustion performance. When the mass fraction of NC increased from 3–10\%, the ignition delay time was shortened from 3.5 ms to 0.3 ms, and the combustion time was prolonged from 46 ms to 64 ms \[6\]. Wang H et al. successfully prepare gel-like NC/ANPs composite particles by electrostatic spray method \[7\], and the mass fraction of NC is 1\% -10\%. The combustion performance test shows that the gel-like NC/ANPs composite particles have stronger combustion behavior than ANPs, and the 10\% NC/ANPs composite particles show the longest combustion time (\(~ 64\) ms) and the shortest ignition delay time (\(~ 0.26\) ms). Yan et al. prepare uniform sized and porous NC/ANPs microspheres by electrostatic spray method. The NC/ANPs microspheres have high pressurization rate and combustion propagation rate \[4\].

Molecular dynamics (MD) simulation is an effective theoretical research mean from atomic scale. It has been successfully applied to explore the properties of ANPs. Alavi uses MD simulation to predict the melting points of ANPs and the simulation results are agreement with the experimental results \[8\]. Much work has been devoted to exploring the sintering of metal nanoparticles by molecular dynamics (MD) simulation \[9–15\]. Song et al. studied two different sizes of nickel nanoparticles through MD simulation \[16\], and found that the sintering of two different sizes of nanoparticles occurred in three stages closely related to surface melting. Liu et al. simulated the non-equilibrium molecular dynamics of the combustion of nano-Al particles coated with ethanol/ether molecules \[17\], and explored the combustion mechanism of coated ANPs.

On the other hand, the sintering of nano powders and metal alloys has also been studied extensively in the experiments \[18–24\]. Sabzi et al. experimentally studied the effects of different sintering parameters on the microstructure evolution \[18\], density and hardness of nano-powder cemented carbide products. A.L. Ahmad et al. established the calculation model of horizontal transverse diffusion of protein in NC film \[25\], and determined the concentration gradient as the driving force of molecular diffusion. Dave T. F. Kuo et al. from Hong Kong City University use First-order model and Intra-Particle Diffusion model to calculate the adsorption and desorption kinetic parameters of NG and 2,4-dinitrotoluene in NC \[26\]. Waldemar A. Trzcinski et al. from Poland Warsaw Institute of Military Science and Technology derived the time-space resolution characteristics of NC-based composite reaction armor explosion through the modified Gurney model \[27\].

As far as we know, the research of NC and nano aluminum powder mixture system is mostly based on experimental methods, which is difficult to directly detect the reaction process and microscopic mechanism in the rapid response stage. Therefore, in order to explore the ignition and combustion mechanism of NC/ethanol/ether coated ANPs, MD simulations are carried out on three different models in this research. Radial distribution function (RDF), average displacement, mean square displacement
(MSD) and other parameters will be quantitatively characterized to reveal the ignition and combustion mechanism of NC/ethanol/ether ternary coating ANPs.

2. Materials And Methods

2.1 ReaxFF-lg long-range correction reaction force field

In the current work, MD simulation is performed using a large-scale parallel atom/molecule simulator (LAMMPS\textsuperscript{[28]}), and visualization post-processing is performed using VMD\textsuperscript{[29]} and OVITO software. The core of MD simulation is the force field. Reasonable force field parameters greatly affect the accuracy and results of simulation. ReaxFF interatomic potential is a reaction force field based on bond-order (BO), which has been successfully applied to computational chemistry\textsuperscript{[30]}. Different from the concept of atomic type in the classical force field, ReaxFF adopts bond-order (BO) formalism to evaluate the interactions between atoms including bond and long-range pair interactions. Eq. (1) presents the total energy in ReaxFF force field:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}}$$

where $E_{\text{system}}$ denotes the total energy of the system. The bond ($E_{\text{bond}}$), overcoordination ($E_{\text{over}}$), undercoordination ($E_{\text{under}}$), lone pair ($E_{\text{lp}}$), valence angle ($E_{\text{val}}$), dihedral twist angle ($E_{\text{tors}}$), van der Waals ($E_{\text{vdW}}$), and Coulomb ($E_{\text{Coulomb}}$) energy terms contribute to the total energy to vary degrees. In addition to $E_{\text{vdW}}$ and $E_{\text{Coulomb}}$ are non-bonding terms, other energies are expressed through BO.

However, the first principle based on density functional theory (DFT) is often used to fit the results in the development of the ReaxFF reaction force field. This method will underestimate the van der Waals force of non-bonding molecules in the calculation process. Therefore, the ReaxFF reaction force field usually underestimates the calculation of equilibrium density when describing molecular systems\textsuperscript{[31]}. In addition, the expression of ReaxFF force field has included the expression of van der Waals interaction. Therefore, it is necessary to introduce a new non-bonding term without affecting the fracture and formation of chemical bonds in the molecule, so that the ReaxFF force field can correct the long-range force and reduce the impact on covalent bonds. Liu et al. use a low-gradient model (Low-Gradient) to correct the long-range effect of density functional calculation\textsuperscript{[32]}. Based on this, the ReaxFF-lg long-range correction reaction force field is developed by using the similar model to correct the long-range effect of the ReaxFF force field. Here, we use the ReaxFF-lg long-range correction reaction force field for simulation calculation. The expression of total energy in ReaxFF-lg force field is described in Eq. (2):

$$E_{\text{system}}^{\text{lg}} = E_{\text{system}} + E_{\text{lg}}$$
where $E_{lg}$ denotes the lg long-range amendments. Its calculation uses the Low - Gradient model. Eq. (3) is the calculation formula of $E_{lg}$:

$$E_{lg} = - \sum_{i,j<i}^{N} \frac{C_{lg,ij}}{r_{ij}^6 + d \cdot R_{ei,j}^6}$$

where $r_{ij}$ is the distance between atoms and $d$, and $R_{ei,j}$ is the Van der Waals interaction equilibrium distance between atoms and $d$, and $C_{lg,ij}$ is the correction coefficient of dispersion force, and is the scale factor.

### 2.2 Simulation system and setup

This study includes two simulation scenarios. For the study on the pyrolysis mechanism of NC single chain discussed in section 3.1, the simulation box measured $25.792 \times 25.792 \times 25.792 \text{ Å}^3$ and the density of NC system was set to be 1.6g/cm3 which is close to the actual density. Figure 1 (a) is a single NC molecular chain model and Fig. 1 (b) is an initial configuration snapshot of amorphous cell pyrolysis. The thermodynamic process of the system is as follows. Firstly, every atom is assigned a velocity to the specified temperature of 5 K in a Gaussian distribution, following which the system is relaxed under the canonical ensemble (NVT) at 5 K for 1 ps to obtain a reasonable configuration. Then, increasing the system temperature to 3000 K slowly at the heating rate of 0.03 K/fs. Finally, lasting for 100ps at 3000 K. The pyrolysis reaction started from the initial stage of heating. Using Berendsen control theory to control the temperature with 20 fs of the temperature resistance coefficient and 0.2 fs of the time step.

For the cases of preparing and burning the ANPs, we use three ANPs models, which are passivated ANPs (sANPs), NC/ethanol/ether coating passivation ANPs (csANPs) and NC/ethanol/ether coating annealing ANPs (cANPs). The simulation box measured $110 \times 110 \times 110 \text{ Å}^3$, ANPs are located in the center of the box and other molecules such as NC, ethanol, ether, oxygen is randomly distributed around ANPs. In our study, the ANP has a typical core-shell structure, which the Al core diameter is 4 nm and the oxide shell thickness is 0.5 nm. According to Liu et al., the melting point of ANPs changes linearly with diameter with diameter more than 2nm \cite{33}. Considering the computational cost, 4nm ANP is sufficient to show the thermodynamic properties. The Al core and alumina shell models are cut from cubic crystals and assembled together. The fusion process which ensures close contact between the core and shell and eliminated surface stress. The basic idea is to relax the passivated particles at 50 K for 1.5 ps to obtain the stable configuration at this temperature; then, the particles are heated to 300 K at the heating rate of 1013 K/fs under the NVT ensemble, and the shell-core structure will gradually integrate during this process. Finally, the passivated particles were relaxed for 200 ps at 300 K to obtain the stable configuration at room temperature. Figure 2 shows the initial configuration and optimized configuration of passivated ANPs.
In order to establish the cANPs model, we need to obtain the annealed ANPs model first. ANPs constructed directly by script commands in LAMMPS are ideal spherical particles composed of FCC cells. To eliminate the edge effect of ANPs, annealing and recrystallization are necessary. The basic idea is that cutting out an aluminum particle with a diameter of 4 nm in the aluminum FCC crystal block, and the whole particles are relaxed at 1300 K to completely melt. Then, to get the annealed ANPs at 300 K as the initial model for subsequent simulation, the molten aluminum clusters were cooled and recrystallized. The whole annealing process is carried out under the NVT with EAM force field. Using the Verlet integral algorithm to solve the Newton motion equation. Using the Nose/Hoover theory to control the temperature. The temperature damping coefficient is selected as 100 fs. The accuracy and efficiency of recrystallization annealing are related to the selection of simulated force field and cooling rate. In our study, we choose 20 K/ns as the cooling rate, and the cooling rate is also verified to have good accuracy and economy \[34\]. Figure 3 shows the ANPs model before and after annealing and the crystal type distribution of the central section.

3. Results And Discussions

3.1 Force field verification of NC thermal decomposition mechanism

The force field used in this study has been proved to be effective for the ethanol-ether-oxygen system \[17\]. However, NC molecules are quite different from ethanol and ether molecules. The chemical properties of ethanol are determined by hydroxyl groups, and ether are characterized by their self-propagating autooxidation (peroxidation) process \[35\]. The main oxidation product of gas phase ether is ether. However, NC molecules will undergo severe self-decomposition at higher temperature (573 K), and the decomposition products are complex. Therefore, it is necessary to simulate the thermal decomposition mechanism of NC molecules in ReaxFF MD simulations. The thermal decomposition reaction simulation settings are shown in section 2.2.

The thermal decomposition temperature of NC single chain is about 1182 K during the heating process \[36\], which is obviously higher than the experimental temperature. It is because the thermal decomposition of NC is limited by the time scale of ReaxFF MD simulation, which has been confirmed in a large number of literatures. Figure 3 shows the variation curve of the number of key product molecules with time in the thermal decomposition process of NC single molecular chain model. The first meteorological product is NO\(_2\), which is consistent with the fact that the -NO\(_2\) base strength measured in the heating process of NC thermal decomposition experiment decreases first. In addition, we found that CH\(_2\)O generated later than NO\(_2\). It is because CH\(_2\)O is the decomposition product of O-NO\(_2\) group on the primary (C-6 position). This is consistent with the experimental results of Wang et al. To see this process more clearly, Fig. 4 shows a snapshot of the local structure of the decomposition process of the primary O-NO\(_2\) group in the simulation. The fracture of O-NO\(_2\) bond and the subsequent formation of CH\(_2\)O can be clearly seen from
Fig. 4. From Fig. 3, we can also find that the number of H₂O, NO, CO₂ and CO molecules began to increase and a small amount of HCOOH formation with the number of NO₂ molecules reaching the peak.

In addition, there are many researchers interesting in the fracture of molecular chains during thermal decomposition of NC. Jutier et al. believed that the thermal decomposition of NC did not necessarily lead to the fracture of the chain \(^{[37]}\). However, Wang et al. believed that along with the denitrication process, the NC macromolecular chain would be decomposed into small molecules. In our study, we captured the fracture of C-O-C bond between NC molecular chains, as shown in Fig. 6. In the pyrolysis process of NC molecular single chain model, the interannular C-O-C bond will be broken, and NC is decomposed into small molecules from macromolecular chains. However, the C-O-C bond breakage in the NC molecular chain is relatively lagging behind, which supports Wang's view that NC macromolecular chains will be decomposed into small molecules along with the denitrication process. It also verifies the accuracy of using ReaxFF force field to simulate NC system.

3.2 Preparation of ANPs with NC/ethanol/ether

As for the establishment of NC/ethanol/ether ternary coating ANPs model, the simulation box measured 120 × 120 × 120 Å³. The annealed and passivated ANPs established in section 2.2 are placed in the center of the box, and the ethanol ether solution molecules are placed in the surrounding area of ANPs. In addition, a vacuum region of 7 Å was set between NC/ethanol/ether solution molecules and ANPs as a buffer region. The volume ratio of ethanol molecule to ether molecule in NC/ethanol/ether solution was 1:1. Considering the ANPs used in our study is small, the number of molecules in NC/ethanol/ether solution needs to be limited within the range that ANPs can withstand, otherwise ANPs are prone to deformation. The specific values are shown in Table 1. The position distribution of ethanol ether solution molecules is completed by the Packmol program \(^{[38]}\), so that it initially forms a nearly uniform mixed solution system.

Table 1 Computational materials science

<table>
<thead>
<tr>
<th></th>
<th>NC</th>
<th>ethanol</th>
<th>ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>sANPs</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>csANPs</td>
<td>3</td>
<td>1000</td>
<td>562</td>
</tr>
<tr>
<td>cANPs</td>
<td>3</td>
<td>1000</td>
<td>562</td>
</tr>
</tbody>
</table>

The whole simulation process is carried out under the NVT ensemble. The ANPs temperature is set at 200 K, which can ignore the thermal vibration of the base atom. All aluminum atoms can retain the interaction with other atoms while fixing the site. The temperature of NC molecular chain was selected as 300 K to ensure the structural stability of NC molecular chain. The temperature of ethanol ether solution was
selected as 500 K, and the higher solution temperature could make up for the limitation of time scale, help us get similar simulation results to those in the experiment (time-scale: ms) within a reasonable time range (time-scale: ps). According to the study of Liu et al., 500 K does not break the results of organic molecules at short time\cite{17}, and can effectively inhibit the formation of hydrogen bonds, which is conducive to the development of coating. Berendsen control theory, which is similar to hot bath, is used in temperature control. The temperature damping coefficient is set to 25 fs. In consideration of the possible of dissociation and bonding in the package process, the time step is 0.25 fs, and the whole simulation lasts 100 ps.

Figure 7 shows the molecular isothermal adsorption curve of NC/ethanol/ether solution coated annealing ANPs and passivation ANPs. In the coating process of passivated ANPs, the adsorption rates of ethanol and ether molecules are always slower than those of annealed ANPs. At the end of the coating, the number of ethanol molecules in the coating layer on the particle surface is about 287, the number of ether molecules is 135, and the ratio of ethanol/ether molecules is about 2.12. The number of ethanol ether molecules in the coating layer of passivated ANPs was significantly less than that of annealed ANPs, indicating that the compactness of coating layer on the surface of passivated ANPs was relatively poor.

In the actual production process, after ANP particles and solution are fully mixed, more organic solutions are removed in the oven. Therefore, at the end of the cycle-coating process, an evaporation-elimination procedure is carried out to eliminate atoms that are not tightly adsorbed on the ANPs. Considering the real ignition environment is about 300 K, the evaporation-elimination simulation is carried out at 300 K. For the first time, manual filter is selected to remove the free complete solvent molecules in the box. Then, put the filtered ANPs in the center of cube box of 120 × 120 × 120 Å$^3$, and to leave sufficient space for the release pressure of the coating layer, the environment was set as a vacuum. After each filtering simulation, the separated solvent molecules were filtered until no molecules were separated and the cycle ended.

Figure 8 shows the molecular numbers of each component in coating layer after each filtering of cANP and csANP. From Fig. 8, we can find that whether csANP or cANP, a large number of ether molecules and a small amount of ethanol molecules are separated from the filtering simulation, and NC molecules remain stable. It is because different molecular structures and adsorption modes, ethanol is chemically adsorbed while ether is physically adsorbed, and ether molecules are more likely to escape in a dry environment. The final composite particles are shown in Fig. 9.

In order to explore the relative structure between organic coating layer and ANPs, Fig. 10 shows the cross-sectional charge distribution and atomic potential energy distribution of the final configuration of cANPs. The Al atoms on the surface of ANPs are strongly positively charged, while the ethanol ether molecules infiltrated into the surface of ANPs are strongly negatively charged. A new bond pair is formed between the Al atoms on the particle surface and the ethanol ether molecules, and the charge transfer also occurs between the bonding atoms. Therefore, this layer is a chemical adsorption layer. From Fig. 10, we can also find that the atomic potential energy of NC/ethanol/ether solution in the chemical adsorption layer is
The outside ethanol ether molecule has a weak charge, indicating that the molecules outside the coating layer interact through non-bonding forces such as Van der Waals force and Coulomb force, so this layer is a physical adsorption layer. The atomic potential energy in the physical cladding layer is high, and the structure is relatively unstable. NC/ethanol/ether solution is still the result of the combination of physical adsorption and chemical adsorption. In addition, the O and N atoms in the NC molecular chain also have strong charge values, which also reveals the hydrogen bond between the ethanol ether molecule and the NC molecular chain.

We calculate the radial distribution functions of different atom pairs, as shown in Fig. 11, to quantitatively study hydrogen bonding between the surface structure of ANPs and NC/ethanol/ether solution of the final configuration ANPs. From Fig. 11 (a), we can find that the surface O atoms of ANPs are mostly located near the Al atom about 1.95 Å, indicating that the outermost Al atoms of ANPs tend to form an alumina layer provided by organic inclusion. The difference between the first peak values of g (Al-EO) and g (Al-DO) curves of NC/ethanol/ether coating was small, indicating that the number of ethanol molecules and ether molecules involved in the chemical adsorption of ANPs surface was similar. In addition, the peak value of g (Al-NO) was relatively low, and the first peak was located near 1.8 Å, indicating that the part of NC molecular chain involved in chemical adsorption was less, and it was more inclined to adsorb on the surface of ANPs by chemical adsorption at one end or one section of the molecular chain. The adsorption strength was stronger than ethanol ether molecules. The other segments were adsorbed on the surface of ANPs by physical adsorption through the traction of the chemical adsorption section and hydrogen bonding. Figure 11 (b) calculated the radial distribution function of H-O and H-N atomic pairs between NC molecular chains and ethanol ether molecules. From Fig. 11 (b) we can find that the ethanol molecule is more likely to form hydrogen bonds with the NC molecular chain. The reason is that the polar-OH in the ethanol molecule and the polar-OH and-ONO$_2$ groups in the NC molecular chain are more likely to form hydrogen bonds through Coulomb interaction. Ether molecule is not easy to form hydrogen bonds in the NC molecular chain, which can prevent large agglomeration and make the NC molecular chain dissolve smoothly to form a homogeneous solution.

To analyze the adsorption behavior of NC molecular chains on the surface of csANPs intuitively, Fig. 12 is the structural snapshot of the final configuration of csANPs. The -NO$_2$ and -OH groups in NC chains are adsorbed on the surface of ANPs, accompanied by the dissociation of -NO$_2$ and -OH groups. The atoms in the separated-NO$_2$ and-OH groups will not be further separated, and it is difficult to penetrate into the passivated ANPs. Therefore, NC molecular chains are still adsorbed on the surface of passivated ANPs by physical and chemical adsorption.

Active Al atom is the main reactant of fuel. After ANP is completely coated, the content of active Al is a very important detection index. Table 2 shows the content of active Al atoms in three models. According to the oxidation degree of Al atom, we divide it into active Al atom, oxidation potential Al atom and oxidation Al atom. For passivated ANPs, the Al atom with charge less than the average charge in the nuclear region is defined as the active Al atom; Al atom whose charge is more than the average charge in the shell is defined as oxidation Al atom; the charge between the average charge in the core region and
shell region is defined as oxidation potential Al atom. For the cANPs model, due to there isn't passivation treatment and the concept of average shell charge is not available, the Al atom whose charge is less than 0.5 is defined as active Al atom. Al atom with charge more than 1 is defined as oxidized Al atom; the charge between 0.5 and 1 is defined as oxidation potential Al atom. Table 2 shows that NC/ethanol/ether coating treatment could reduce the content of oxidation Al atom. However, no matter which model, the content of unoxidized Al atom is above 70%.

Table 2 The Al atomic activity for sANPs, csANPs and cANPs.

<table>
<thead>
<tr>
<th></th>
<th>active Al atom</th>
<th>oxidation potential Al atom</th>
<th>oxidation Al atom</th>
</tr>
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<tbody>
<tr>
<td>sANPs</td>
<td>27.4%</td>
<td>42.6%</td>
<td>30.0%</td>
</tr>
<tr>
<td>csANPs</td>
<td>22.1%</td>
<td>51.8%</td>
<td>26.1%</td>
</tr>
<tr>
<td>cANPs</td>
<td>52.00%</td>
<td>38.20%</td>
<td>9.80%</td>
</tr>
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</table>

3.3 MD simulations of heating and combustion processes

3.3.1 Heating period

After the evaporation-elimination procedure, the ignition and combustion stage can be carried out. In order to verify the effect of NC/ethanol/ether coating layer on the heating and combustion performance of ANPs, we set up three combustion models of sANPs, csANPs and cANPs. In the heating period, the three ANPs models were put in a 110 × 110 × 110 Å³ box, and 1200 O₂ molecules were randomly put around the ANPs. The specific parameters of the heating model are as follows: Firstly, the heating system is relaxed at 300 K, and then the system temperature is increased to 1000 K in 70 ps under the NVT ensemble. According to the ignition characteristics of ANPs, 1000 K is enough to ignite ANPs.

At present, although there are many controversies about the ignition mechanism of ANPs, the diffusion movement of atoms is considered to be one of the important ideas about the ignition mechanism of ANPs [39, 40]. Figure 13 calculated the mean square displacement curves of ethanol, ether and NC atoms during heating period of csANPs and cANPs. At the initial heating period (~ 20 ps), the atomic mobility of each component increased slowly, and the coating layer won't parsing clearly at low temperature. After 20 ps, the atomic mobility of ether and ethanol began to increase rapidly. At this time, the ether and ethanol molecules began to parsing and diffuse rapidly, while the parsing and diffusion of NC lagged significantly. In addition, ether molecules showed higher mobility during ignition, indicating that the parsing and diffusion of ether were earlier than ethanol. Due to the strong of physical adsorption in csANPs coating layer, csANPs coating layer atoms have higher mobility than cANPs.

In order to observe the diffusion movement of each component atom intuitively in heating period, Fig. 14 shows the central section configuration diagram of sANPs, csANPs and cANPs systems at different
ignition times. At the initial heating period (20 ps), O$_2$ molecules adsorbed on the surface of ANPs gradually, but it was difficult to penetrate the oxide/coating layer. Because of coating layer, csANPs and cANPs can adsorb more O$_2$ molecules around them than sANPs. It means organic coating layer was beneficial to the adsorption of O$_2$ molecules. With the increase of temperature (20–40 ps), the Al core atoms begin to melt, and the melting temperature of Al core decreases significantly. With the melting of Al core, the O atom in the oxide shell (sO) begins to diffuse inward, while the Al atom in the aluminum core (cAl) begins to diffuse outward. As for cANPs, due to without oxide layer, organic coating layer atoms began inward diffuse at this stage, which makes the surface structure of ANPs looser. At 40–70 ps, the molecules ethanol and ether molecules in the coating layer were obviously exfoliated, while the NC macromolecular chain was still around the surface of ANPs although it showed a certain degree of detachment. With the detachment of coating layer, O$_2$ molecules were further adsorbed on the surface of ANPs even diffused into ANPs, which promoted the ignition of ANPs.

The pyrolysis behavior of NC molecular chains during heating period is also interesting. Figure 15 shows the change rates of C-O and N-O bond pairs number with time in the heating period of NC. At about 25 ps (549 K), the NC molecular chains in the coating layer of csANPs and cANPs began to pyrolysis. NC pyrolysis also releases heat, increases the surface temperature of ANPs particles which can shorten the ignition time of ANPs.

Figure 16 shows the MSD curves of cAl atoms during heating period of sANPs, csANPs and cANPs. At the initial ignition stage, the MSD curve of cAl atom in csANPs and cANPs was lower than that of sANPs, which means NC/ethanol/ether coating can improve the stability of active Al core atoms at low temperature. After that, the MSD curves of cAl atoms in csANPs and cANPs increased rapidly, and exceeded sANPs at about 22 ps and 15 ps respectively. With the increase of temperature, the active Al core in csANPs and cANPs showed higher atomic mobility. High atomic mobility makes the active cAl atoms in ANPs diffuse to the surface and react with external O$_2$ molecules faster, which also reveals one of the reasons why NC/ethanol/ether coating layer can shorten the ignition delay of ANPs.

The direct contact reaction of external O$_2$ molecules with active Al atoms in ANPs is usually considered to be an important indicator of ANPs ignition. Figure 17 shows the variation of the O atoms' number in the range 2 Å of ANPs surface during heating period. At the beginning of ignition, the oxygen adsorption amount of csANPs and cANPs was much lower than sANPs. With the increase of temperature, the oxygen adsorption amount of csANPs and cANPs quickly rising and exceeded the sANPs. Which further proof that NC/ethanol/ether coating will inhibit external O$_2$ molecules contact with ANPs at low temperature, and promote external O$_2$ molecules adsorption and reaction with ANPs at high temperature.

Figure 18 shows the radial distribution function of cAl-eO atom during ignition period. The RDF curves in sANPs, csANPs and cANPs systems have the same trend over time. From Fig. 18, the first peak is about 1.9 Å, corresponding to the Al-O bond length. At 0–20 ps, the first peak value of csANPs was significantly lower than sANPs, indicating that the coating inhibits the external O$_2$ molecules contact with Al core
atoms at low temperatures. With the increase of temperature, the first peak value of csANPs increased rapidly and exceeded sANPs. It is because at low temperature, the O$_2$ molecules adsorbed by the coating layer react rapidly with the reaction sites released on the surface of ANPs after coating layer resolution, which also reveals another important mechanism of coating layer shortening the ignition delay of ANPs. Finally, with the increase of temperature, RDF curve appeared obvious second and third peaks. It shows that the reaction between O$_2$ and cAl atoms gradually diffuses inward, forming a long-range ordered oxidation structure.

3.3.2 Combustion period

In the combustion period, the simulation box is expanded to $150 \times 150 \times 150$ Å$^3$, and the ignition process parameters are same with 3.3.1. Due to the research background is the improvement of aluminum-containing propellant, the combustion temperature of aluminum-containing propellant in the combustion chamber can stabilized at about 3000 K continuously. Therefore, after the heating period, the ensemble is changed from NVE to NVT, and the simulation temperature is set at 3000 K$^{[41]}$. The three models are stabilized at 3000 K for combustion simulation.

Figure 19 shows the rectangular central cross-sectional views along the Y-axis and the atomic displacement scatter plots at different times of the three systems' constant-temperature combustion at different times (with the atomic positions 5 ps before this time as a reference). The width of rectangular section is 15 Å, the transverse coordinate of scatter plot corresponds to the radial distribution along the Y axis, and the ordinate represents the absolute displacement of each atom before 5 ps. According to the absolute value of atomic displacement in 5 ps, the displacement scatter diagram of combustion system can roughly divide into gas phase region and solid-liquid phase region roughly.

For sANPs and csANPs, because 3000 K is much higher than the melting point of Al core and oxide shell, the cAl atom in the central region and the sO atom in the oxide shell diffuse rapidly and the shell-core structure completely disappear at 10 ps. Figure 19 (a) shows that the displacement of cAl and sO atoms tend to the same level at 10 ps, indicating that there is an almost uniform distribution of cAl-sO mixed configuration in sANPs. In this stage, the sAl atoms are still mainly distributed in the outer oxide shell region, resulting the movement ability of the external O$_2$ molecules is strong, it is mainly adsorbed in the oxide shell region, which is difficult to penetrate into the inner layer of sANPs. At this stage, due to the inward diffusion of sO, releasing more partial coordination of sAl, which makes it exhibit excellent oxidation potential. After 20 ps, sO and eO atoms began to diffuse to the inner region of the particles, and the combustion began to propagate inward and formed a diffusion-dominated reaction zone. Finally, sO and eO atoms propagate to the core area of particles, and all components gradually tend to be uniform. In addition, after 20 ps, although the displacement of each component in sANPs also gradually tends to be consistent, the number of external O$_2$ molecules continues to decline. So, at this time, sANPs enter the uniform combustion stage, and the combustion is still ongoing. Due to the influence of reaction temperature, the whole sANPs finally showed a uniform liquid structure. From the Fig. 19 (b), for csANPs, the NC/ethanol/ether coating layer was rapidly desorbed at 3000 K, most of which diffused to the gas
phase region, and only a small part was directly involved in the surface reaction of csANPs and reacted with sAl atoms. Before 10 ps only a few O\textsubscript{2} molecules can react with sAl atoms, however the combustion process of particles will not be slowed down due to the NC molecules get heat and rapid pyrolysis releases heat. After 20 ps, sAl atoms began to diffuse to the inner region, and also led to the inward diffusion of eO and organic atoms (mainly EO and DO atoms), entering the combustion propagation stage. Compared with sANPs, the solid-liquid phase structure of csANPs is more complex due to the participation of NC/ethanol/ether coating layer components. At the later stage of combustion, csANPs transformed into Al-O-C mixed structure. In the central section configuration diagram at 60 ps, C atoms are mainly distributed in the outer layer of particles, forming a large number of Al-C bonds. It is also consistent with the reports on the formation of carbon inclusion products in Al-containing propellants combustion experiments\textsuperscript{[42]}. In addition, the atomic displacement scatter plot also shows that the displacement of each component in the csANPs system doesn't decrease in the sANPs system at the later stage of combustion, but shows an upward trend, which further indicates that the diffusion and pyrolysis of NC/ethanol/ether coating layer will accelerate the multiphase reaction and promote csANPs combusting more sufficient. From the Fig. 19 (c), the combustion process of cANPs is much faster than sANPs and csANPs. Due to the Al atoms in the oxidation shell provided by cANPs still have strong oxidation potential, the outside Al atoms outside react violently at the beginning of combustion, resulting in a rapid decrease in the density inside the particles, and even appear a cavity phenomenon at 10 ps. In addition, the H atoms infiltrated in the coating process will generate H\textsubscript{2} molecules in ANPs firstly, and then release to the gas phase region to participate in gas phase combustion. Because cANPs don't have the oxide layer, the atom diffusivity is stronger, showing higher combustion propagation rate and combustion efficiency. At the late combustion stage, cANPs were also transformed into Al-O-C mixture, which was consistent with csANP. The diffusion and pyrolysis of NC/ethanol/ether coating layer accelerate the multiphase reaction and improve the combustion performance of cANPs.

In order to further quantitatively analyze the ANPs component distribution in the combustion process, Fig. 20 shows the number of O atoms and C atoms adsorbed with time in the 2 Å range of Al atom. At the early stage of combustion, the O atom adsorption rate of sANPs and cANPs was almost the same, slightly faster than csANPs. The reason is that the sO atoms in the sANPs oxidation shell diffuse inward rapidly at the early stage of combustion, and the Al-rich environment is formed on the particle surface, thus adsorbing the external O\textsubscript{2} molecules rapidly and generating oxidation reaction. However as for cANPs, due to the cladding layer involved in the surface reaction, the initial O\textsubscript{2} adsorption rate slowed down. As for cANPs, due to the insufficient coordination number of Al atoms in the oxide layer, they also have the power to absorb external O\textsubscript{2} molecules rapidly. On the other hand, at the end of combustion, the oxygen adsorption rate of sANPs tends to be constant, while the adsorption rate of cANPs begins to decrease, and csANPs even begin to release some adsorbed O atoms. It is because that the further combination of Al-C bonds in the later stage, occupying the outer space of ANPs. The C atom adsorption curve also shows that csANPs and cANPs adsorb large amounts of C atoms at the early stage of combustion and increase steadily at the later stage. Therefore, C atom not only is a high-quality
additional fuel source for gas phase reaction, but also participates in the solid-liquid phase combustion reaction outside ANPs directly.

Figure 21 shows the potential energy curves of sANPs, csANPs and cANPs during combustion. Compared with sANPs, the decline rate of potential energy curve in the early stage of the system was similar for csANPs and cANPs, and higher than sANPs significantly. It indicated that csANPs and cANPs had a more intense combustion reaction. The slope of the potential energy curve of the sANPs tended to be constant in the late stage, and entered a stable and uniform combustion stage. On the other hand, the interesting thing is that the potential curves of csANPs and cANPs tend to flatten at about 55 ps and 30 ps respectively, while the potential curves of cANPs begin to fall again at about 65 ps. The reason is that the existence of NC/ethanol/ether coating layer causes the gas phase combustion in csANPs and cANPs systems, and the gas phase combustion in cANPs system starts earlier. The breaking of the bonds of organic molecules such as NC leads to the system potential energy gradual even increase, while the large generation of gaseous molecules leads to the system potential energy continuous decrease. In addition, the potential energy curves of csANPs and cANPs also revealed that the existence of NC/ethanol/ether coating layer not only brought the occurrence of multiphase reactions, but also increased the reaction time of ANPs combustion system. It will make the combustion of ANPs more fully and the energy release time longer, also improving the application potential in propellants.

4. Conclusions

In this study, we used MD simulations to simulate three models: passivated ANPs, NC/ethanol/ether coating passivated ANPs and NC/ethanol/ether coating annealed ANPs. The analysis was carried out from the organic coating process to the ignition and combustion stages. The simulation results show that the ReaxFF-lg long-range correction reaction force field can not only capture the accurate changes of products, but also accurately capture the formation and fracture of bonds in the reaction process. During the pyrolysis of NC single-chain molecules, the C-O-C bond between the rings will break. And NC will decompose from the macromolecular chain into small molecules, while the C-O-C bond fracture in the NC molecular chain is relatively lagging behind, which supports the research view of Wang et al., and also proves the applicability of the ReaxFF-lg long-range correction reaction force field in this study. In the preparation of NC/ethanol/ether coated ANPs model, we found that NC/ethanol/ether solution formed a dense coating layer on the surface of annealed ANPs and passivated ANPs, which was the result of the combined action of physical and chemical adsorption. The inner side of the coating layer is a chemical adsorption layer composed of surface Al atoms and coating solution atoms. The outer side of the coating layer is a physical coating layer composed of organic molecules and residues under the action of Coulomb force and van der Waals force. In the ignition and combustion simulation of the three models, we found that at low temperature, the coating layer blocked the contact between the active Al core atoms and the external O$_2$ molecules, and increased the O$_2$ molecular density around ANPs through adsorption. With the increase of ignition temperature and the accumulation of NC pyrolysis energy release, the NC/ethanol/ether coated ANPs have higher surface temperature, and the active Al atoms in the aluminum
core can diffuse to the particle surface faster. At the same time, the desorption and diffusion of organic coating layer exposed more reaction sites, and the high-density O$_2$ molecules around ANPs were easier to adsorb to the surface for reaction. Thus, NC/ethanol/ether coated ANPs have shorter ignition delay and lower ignition temperature. In the combustion stage, ANPs experienced surface oxidation/core melting diffusion, combustion inward propagation and uniform combustion three stages. After combustion beginning, the NC/ethanol/ether coating layer desorbs and diffuses to the gas phase region rapidly, and a small part is involved in the surface oxidation of ANPs directly. The energy released by NC pyrolysis and gas phase reaction promotes the atom diffusion in ANPs and accelerates the combustion propagation rate. In addition, the C atoms in the coating layer is not only a high-quality additional fuel source for the gas phase reaction, but also participates in the solid-liquid phase combustion reaction outside ANPs directly, increasing the combustion time and efficiency of ANPs.

Declarations

Availability of Data and Materials

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

CRediT authorship contribution statement

Xin Jin: Writing - editing. Lei Wang: Writing - original draft & review & editing. Pingan Liu: Conceptualization, Methodology, Resources, Funding acquisition. Penghua Sui: Formal analysis, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References


Figures
Figure 1

(a) NC single molecular chain model, (b) NC amorphous cell pyrolysis simulation snapshot of initial configuration structure.

Figure 2

(a) the initial configuration and (b) optimized configuration of core-shell ANP used in this paper. The Al core diameter 4 nm and the thickness of oxide shell is 0.5 Å. Atoms are colored by atom type: blue and dark gray for shell and core Al atoms, yellow for O atoms.
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(a) Initial model (b) melting model (c) particle configuration of annealing model and (d) initial model (e) melting model (f) crystal type distribution of particle center section of annealing model.
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Time-dependent curves of molecular number of key products during thermal decomposition of NC single molecular chain model.

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Snapshot of thermal decomposition process of O-NO$_2$ bond.
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**Figure 17**

The adsorption quantity of eO atoms changing with time during heating period for sANPs csANPs and cANPs.
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Figure 19

The snapshots of the rectangular central section along the Y axis and the atomic displacement scatter plot during the constant temperature combustion period. (a) sANPs (b) csANPs and (c) cANPs. Atomic coloring by atomic type. Grey: cAl atoms, yellow: O atoms, blue: sAl atoms, black: C atoms, purple: eO atoms, green: H atoms, red: O atoms.
Figure 20

Curve of atomic adsorption quantity with time during combustion for (a) sANPs, csANPs, cANPs and (b) csANPs, cANPs.

Figure 21

Curve of potential energy change during combustion for sANPs, csANPs and cANPs.