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Passivation of aluminium particle and its effects in solid propellants: a ReaxFF study

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Abstract

Molecular dynamics simulations have emerged as a powerful tool for studying the passivation of metal surfaces by oxygen, providing insights into the mechanisms underlying this process at the atomic scale. In this study, we have used molecular dynamics simulations to investigate the passivation of an aluminium particle by oxygen, as aluminium is one of the most used metallic additives of solid rocket propellants. Specifically, the interaction between a single aluminium particle and oxygen molecules in a controlled environment. The simulations were performed using ReaxFF forcefield and involved the use of a variety of analytical techniques to analyse the results. The results of the simulations showed that the passivation of the aluminium particle by oxygen occurred through a sequence of reactions. Initially, the oxygen molecules adsorbed onto the surface of the particle, forming oxygen atoms that diffused into the bulk of the metal. This diffusion led to the formation of an oxide layer on the surface of the particle, which effectively passivated the underlying metal. Based on the behaviour observed, the passivation process was highly dependent on the temperature of the system. At low temperatures, the formation of the oxide layer was slower and incomplete, leading to the formation of a highly disordered oxide layer. At higher temperatures, the oxide layer formed much more quickly and was much more ordered, with a crystalline structure. Overall, the study provides valuable insights into the passivation of aluminium particles by oxygen, highlighting the importance of molecular dynamics simulations in the study of materials science. In particular, the results of the study shed light on the mechanisms underlying the passivation process and suggest that temperature plays a critical role in determining the structure and properties of the resulting oxide layer.

Keywords: aluminum, passivation, reactive molecular dynamics

Nomenclature
A: frequency factor
E_a: activation energy
E_{bond}: bond energy
E_{over}: over-coordinated atom in the energy contribution
E_{under}: under-coordinated atom in the energy contribution
E_{val}: valence angle term
E_{pen}: penalty energy
E_{tors}: torsion energy
E_{conj}: conjugation effects to molecular energy
$E_{vdWaals}$: nonbonding van der Waals interactions
$E_{Coulomb}$: Coulomb interactions

1. Introduction

Aluminium (Al) and its alloys have been indispensable materials in various industrial applications, owing to their exceptional combination of lightweight, mechanical strength, and corrosion resistance. Solid propellants, in particular, have harnessed the energy release from the combustion of aluminium particles with oxidizers to propel spacecraft and launch vehicles into space. However, its surface reactivity, particularly in aggressive environments, poses a significant challenge in ensuring the long-term stability and performance of aluminium-based components, as the surface passivation may decrease the reactivity of Al particles [1], thus reducing the energy release and the propellant combustion performance. Although the passivation layer can improve the stability of aluminium particles, it reduces their energy density. With the decrease of particles size, the specific surface area increases, and the presence of passivation layer bring significant influence: the proportion of active aluminium decreases obviously [2].

Passivation is a crucial surface modification process that enhances the resistance of the material to environmental factors, such as oxygen, moisture, and aggressive chemicals. This protective layer, typically in the form of alumina (Al_2O_3), acts as a barrier between the substrate and the surrounding environment, mitigating corrosion and ensuring the material's longevity. The understanding of the mechanisms governing passivation is fundamental not only for extending the lifespan of products but also for advancing applications in diverse fields, including aerospace, automotive, and electronics.

Reactive Molecular Dynamics (RMD) simulation has emerged as an invaluable means to investigate the complex atomic-scale processes involved in aluminium

passivation. RMD enables the exploration of chemical reactions, bond formation, and structural transformations at the nanoscale, offering insights that are often challenging to attain through experimental techniques alone. This simulation technique can elucidate the intricate dynamics of Al_2O_3 growth, dissolution, and the influence of various factors such as temperature, pressure, and the presence of impurities.

In this work, we study the aluminium passivation by leveraging the capabilities of Reactive Molecular Dynamics simulation. Our study aims to unravel the intricate interplay of atoms and molecules at the aluminium surface during the passivation process. By simulating the formation and evolution of the protective oxide layer, we seek to provide a comprehensive understanding of the kinetics involved in passivation.

2. Methodology

An aluminium particle passivation was simulated using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [3,4]. The resolution of MD equations through the ReaxFF model [5] of interatomic interactions provides a complete description of the temporal evolution of the system, which includes the formation and breaking of chemical bonds. In this force field, the general energy function takes the following formulation:

$$\text{Esystem} = \text{Ebond} + \text{Eover} + \text{Eunder} + \text{Eval} + \text{Epen} + \text{Etors} + \text{Econj} + \text{EvdWaals} + \text{ECoulomb} \quad (1)$$

The simulation was performed using a spherical aluminium particle surrounded by oxygen molecules (Fig. 1), so the surface reactions can be closely observed, at different temperatures. The particle with 10 Å radius is composed of 252 Al atoms, resulting in a density of 2.7 $g.cm^{-3}$ (literature density: 2.70 $kg.m^{-3}$ [6]), and 200 O_2 molecules are surrounding the particle.

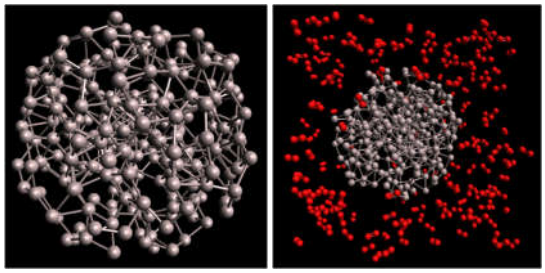

Fig. 1. Al particle (left) and Al particle surrounded by oxygen (right)

The system was minimized using low temperature (5 K) molecular dynamics and then equilibrated at 298 K with constant number of atoms (N), constant volume (V) and control of the temperature (T), denoted as NVT ensemble, during 20-40 ps. For the production phase, the NVT ensemble was also employed, considering a timestep of 0.1 femtoseconds (fs). The total simulation time (production phase) was 100 ps for temperatures in the range of 300-1500 K. The temperatures were controlled by the Berendsen thermostat, with temperature damping constant of 100 fs.

3. Results and Discussion

The aluminium particle was simulated in an oxygen-rich environment at different temperatures. Fig. 2 presents the particle at the end of the simulation at 300 K, showing the high amount of oxygen atoms in the surface (red). It is already known that the oxidation of aluminium surface is fast, but its effects on combustion lack some deeper understanding.

During the last decades, solid propellant formulations were optimized and enhanced, and one of the aspects modified was the particle size of the components. Nano-aluminium has been widely tested and used, as the increase on the surface area leads to an increase in the combustion efficiency and also to an increase in the burning rate.

However, higher surface areas may also react faster to oxygen present in the atmosphere, if the process is not well controlled or if the material is exposed to the environment. Usually, there are companies which produce the nanoparticles with some kind of plasticizers or compounds that prevent re-agglomeration or oxidation, but in most cases, the material is pure.

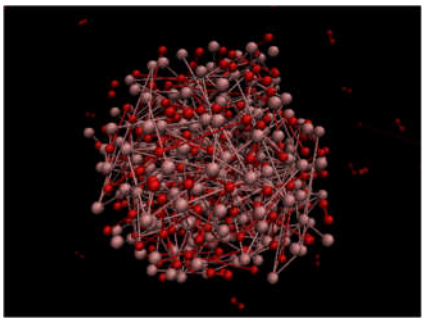

Fig. 2. Al particle at the end of the simulation (300 K)

Based on the simulation results, the velocity of oxygen incorporation in the metal surface is very high, as the process is exothermic and spontaneous. Higher temperatures accelerate the passivation process, and the overall energy of the system is lowered, i.e., the system becomes more stable with the oxide layer. Figure 3 shows the amount of oxygen molecules consumed over time, in different temperatures. This decrease in the number of molecules is directly related to the bond with Al atoms in the particle surface.

During the simulation, not only alumina was formed, but a high number of intermediates as well. If enough time is given, a symmetrical oxide layer shall be observed in the system.

At 1500 K, more than half of the oxygen was consumed during the simulation. From 200 molecules to 73, some of the oxygen was observed even inside the aluminium particle, showing that gas diffusion at this temperature is spontaneous. This could also indicate that some species could be used to protect the aluminium from oxidation by diffusion.

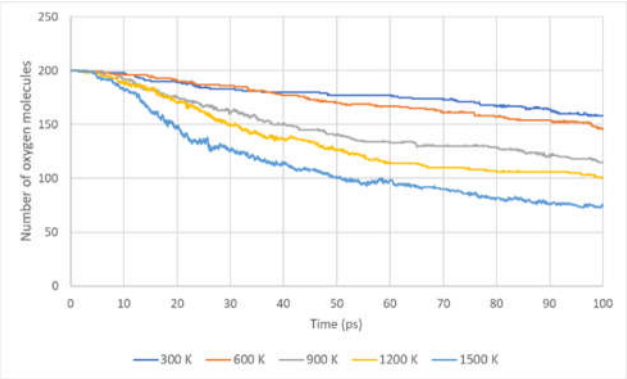

Fig. 3. Number of oxygen molecules over time in different temperatures

Regarding the system's energy dynamics, as depicted in Fig. 4, we present a comprehensive view of the temporal evolution of total energy across all simulations. At the initial stages, we observe a notable surge in energy, attributable to the dynamic reorganization of particles within the system, accompanied by a modest expansion effect. This surge can be directly attributed to the system's initial equilibration at 300 K, where the particles respond energetically to the transition from their initial state to the targeted operating temperature.

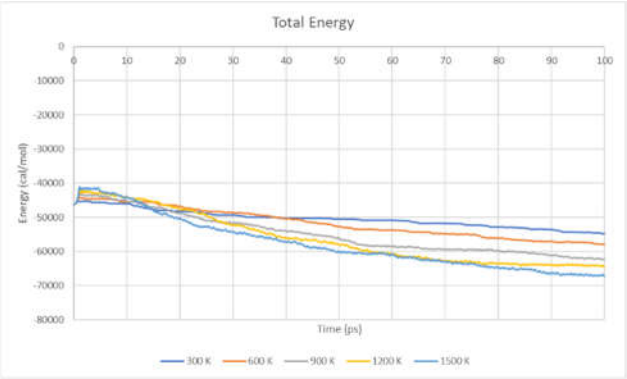

Fig. 4. Total energy of the system over time for different temperatures

At the end of the simulations, as observed in Fig. 4, at 300 K, the energy of the Al particle decreases approximately 20 %, while at 1500 K, the decrease is approximately 48%. If the standard enthalpy of formation of alumina is −1675.7 kJ/mol [7], therefore the energy loss when using room temperature passivated aluminium is at least 335 kJ/mol. Considering that the characteristic velocity is proportional to the flame temperature, the negative effect of the passivation is directly observed in the ballistic properties. Therefore, higher passivation levels may lead to severe differences in performance of solid rocket formulations.

Regarding the kinetics of the aluminium oxidation to alumina, the RMD results allowed the production of an Arrhenius plot (Fig. 5). As observed, there is a good linearity of the results, and the activation energy and the frequency factor are calculated. To increase the correlation factor (R^2), more simulations at different temperatures should be done.

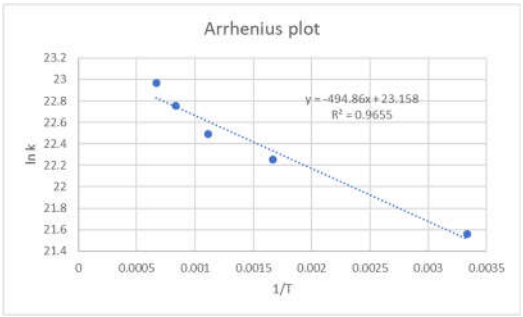

Fig. 5. Arrhenius plot for calculating the kinetic parameters

Ea = 4.11 kJ/mol

A = 1.14E+10

An activation energy of only 4 kJ/mol, a mere fraction of the typical energy barriers encountered in chemical reactions, serves as a compelling rationale for understanding the spontaneity characterizing the passivation process. In essence, this minimal activation energy requirement underscores the effortless ease with which aluminium atoms and oxidizing species engage in the passivation, rendering the overall process highly favourable and practically immediate, as even modest thermal fluctuations readily supply the necessary energy to initiate this self-protective mechanism.

4. Conclusions

In conclusion, our comprehensive exploration of aluminium passivation in solid propellant formulations by reactive molecular dynamics simulations, has provided valuable insights into the intricate dynamics of this critical process. The possible energy loss during aluminium-based solid propellant burning processes may reach more than 20%, due to the passivation of the metallic material. This shows the necessity of protecting and treat the material prior to its application in the formulations. An activation energy of 4 kJ/mol was calculated, elucidating the rapidity and spontaneous nature of aluminium passivation. This minimal energy

barrier not only accelerates the formation of protective oxide layers but also highlights the thermodynamic favourability of the process.

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