ReaxFF Molecular Reactive Dynamics on Surface passivation of Al and AlH_3

Wenya Wu[a], Aoning Cao[b], Jiasheng Shi*

China Fire and Rescue Institute, Beijing 102202, China

[a]1209425489@qq.com

[b]1714045738@qq.com

*Corresponding author. Email address: 18610962257@163.com

Abstract. Use density functional theory to fit a ReaxFF reaction force field which is applicable to CHONAl systems. By applying this reaction force field, molecular reactive dynamics on surface permeation of Al and AlH_3 are performed. Results show that the thickness of passivation layer of Al and AlH_3 are obviously reduced under lower temperature. The thickness of passivation layer of Al is 0.9 nm and 1.5 nm when temperature is 200 K and 400 K, respectively. The passivation layer of AlH3 contain Al(OH)3 of 60% mass fraction at lower temperature, and the Al(OH)3 dehydrates and generates Al2O3 at 400 K).

Keywords: Molecular reactive dynamics; ReaxFF force field; Al; AlH_3; passivation..

1. Introduction

Aluminum-containing explosives are widely used in underwater thrusters, thermobaric munitions, etc., to improve acceleration performance, explosive heat, and extend energy release time. In the practical application of micron/nanometer aluminum powder, due to the specific surface area effect, usually the smaller the particle size, the higher the activity. However, when the particle size is reduced to the nanometer scale, the proportion of the passivation layer (about 1-3 nm thick)[1-3] in the fuel Al cannot be ignored. The passivation layer is a less active material layer formed on the surface of Al after contact with an oxygen-containing atmosphere (such as air). The presence of the passivation layer protects the active fuel inside the particles, but seriously reduces the performance of the ultrafine nanometer Al powder (particle size 50-200 nm). For example, the explosive heat[4], underwater energy release[5] and propulsion capacity[6] of nano-sized aluminum powder have no advantages compared with the micron aluminum powder explosive. In order to improve the properties of ultrafine nanometer Al powder, the thickness of oxide layer must be reduced. Therefore, it is necessary to understand how passivation occurs and explore ways to reduce the thickness of the passivation layer.

Compared with experimental methods, ab initio molecular reaction dynamics simulation has a unique advantage in describing chemical reaction processes, because it can track the quantities and configurations of reactants and products in real time with high accuracy, and provide chemical interpretation of the final reaction results. But it also has the corresponding shortcomings, such as the small scale of the simulation system, the simulation time is short. For the first shortcoming, we use the first principles to fit the ReaxFF reaction force field, and then use the field to simulate the molecular reaction dynamics of nanoscale systems. Compared with the first principles density functional method, the scale of the simulation system is increased from 100-200 atoms to 5000-10000 atoms on the basis of the basic unchanged simulation accuracy. For the second disadvantage, we achieve an approximation of long-term passivation by increasing the oxygen concentration.

The thickness, density and composition of the passivation layer, as well as the evolution of gaseous fragments outside the layer over time, were revealed through molecular reaction kinetics simulations of 100 ps at 200 K, 300 K and 400 K, respectively, for the designed Al/O2 and AlH3/O2 models (FIG. 1). This process information is used to investigate the process of passivation reaction and to evaluate the effect of temperature on the passivation of Al and AlH3 surfaces. The box sizes of Al surface and

AlH3 surface models were 40.82 A ×40.82 A ×181.52 A and 27.24 A ×33.26 A ×186.24 A, and the number of atoms and molecules were 4000 Al/1296 O_2 and 1320 AlH_3/1296 O_2, respectively.

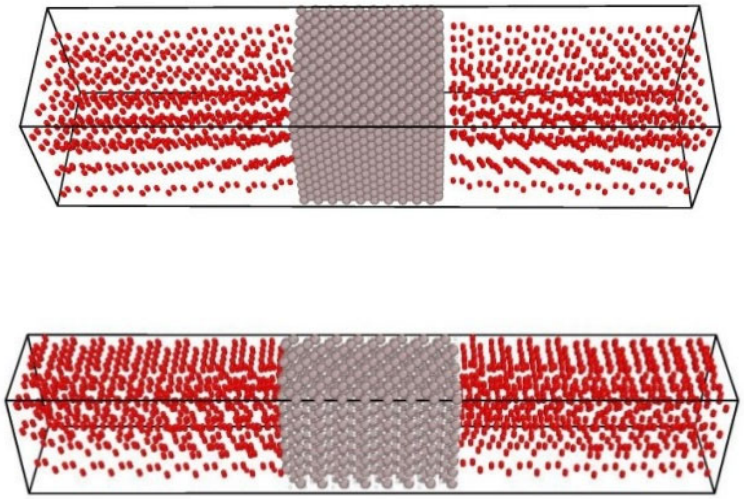


Fig. 1 Designed Al/O2 (a) and AlH_3/O_2 (b) models.

2. Calculation and simulation methods

The potential energy surface of Al-C, Al-N, Al-O and Al-H bond interaction, phase critical Angle and dihedral Angle potential energy surface were optimized by density functional theory at B3LYP/6-31++G** level. The ZORC relativistic correction is applied to the Al element. The results are used to fit the ReaxFF reaction force field. It has been verified that the density and average bond length of aluminum carbide, aluminum nitride, aluminum hydride, alumina and explosive crystals simulated by the reaction force field are compared with the calculated results of PBE method, as shown in Table 1. Experimental values in the table were obtained from literature [7-9].

Table 1 Compared the fitting reaction force field optimized relative crystal density and average bond length with the PBE method.

Crystal	Density					Bond length					
	Expt.	GGA/PBE	PBE-err (%)	Reax	Reax-err (%)	Type	Expt.	GGA/PBE	PBE-err (%)	Reax	Reax-err (%)
Al_2O_3	4.08	3.83	-6.24	4.27	4.67	Al-O	1.8993	1.9355	1.91	1.8760	-1.22
AlH_3	1.63	1.68	3.30	1.49	-8.46	Al-H	1.7051	1.7002	-0.29	1.7922	5.11
AlN	3.15	3.26	3.42	3.29	4.25	Al-N	1.9165	1.8889	-1.44	1.8968	-1.03
Al_4C_3	3.00	2.97	-1.11	2.95	-1.68	Al-C	2.0513	2.0529	0.08	2.0428	-0.42
Al	2.73	2.73	0.09	2.74	0.37	Al-Al	2.8524	2.8336	-0.66	2.8463	-0.21
TKX-50	1.91	1.66	-13.26	1.74	-9.09	C-N	1.3340	1.3903	1.97	1.3599	1.94
CL-20	1.91	1.63	-14.74	1.74	-8.99	N-N	1.4543	1.4769	1.55	1.5306	5.24
RDX	1.87	1.70	-8.98	1.72	-7.79	C-H	1.0753	1.1109	3.32	1.1115	3.37
HMX	1.96	1.80	-8.22	1.76	-10.36	N-O	1.2286	1.2334	0.40	1.2953	5.43
MAE			6.59		6.18				1.54		2.66

As can be seen from Table 1, the mean absolute error (MAE) of density and mean bond length is comparable to GGA/PBE method. The results show that the ReaxFF reaction force field can effectively simulate the CHONAl system. Using the obtained reaction fields, the molecular reaction kinetics of Al/O_2 and AlH_3/O_2 models were simulated at 100 ps at 200, 300 and 400 K respectively under the NVT canonical ensemble. The time step is set to 0.25 fs.

3. Results and discussion

3.1 Thickness and density of passivation layer.

The thickness and density changes over the simulation time are shown in Figure 2. It can be seen that the passivation layer thickness of Al/O_2 system ranges from 0.9-1.5 nm and varies greatly with temperature. The passivation layer thickness of AlH_3/O_2 system ranges from 1.0-1.3nm, and changes little with temperature. The passivation layers of both of them are thinner at low temperature, indicating that low temperature can reduce the passivation layer thickness, especially Al. On the other hand, the passivation layer density of Al/O_2 system is basically not affected by temperature, while the passivation layer density of AlH_3/O_2 system is slightly larger at high temperature.

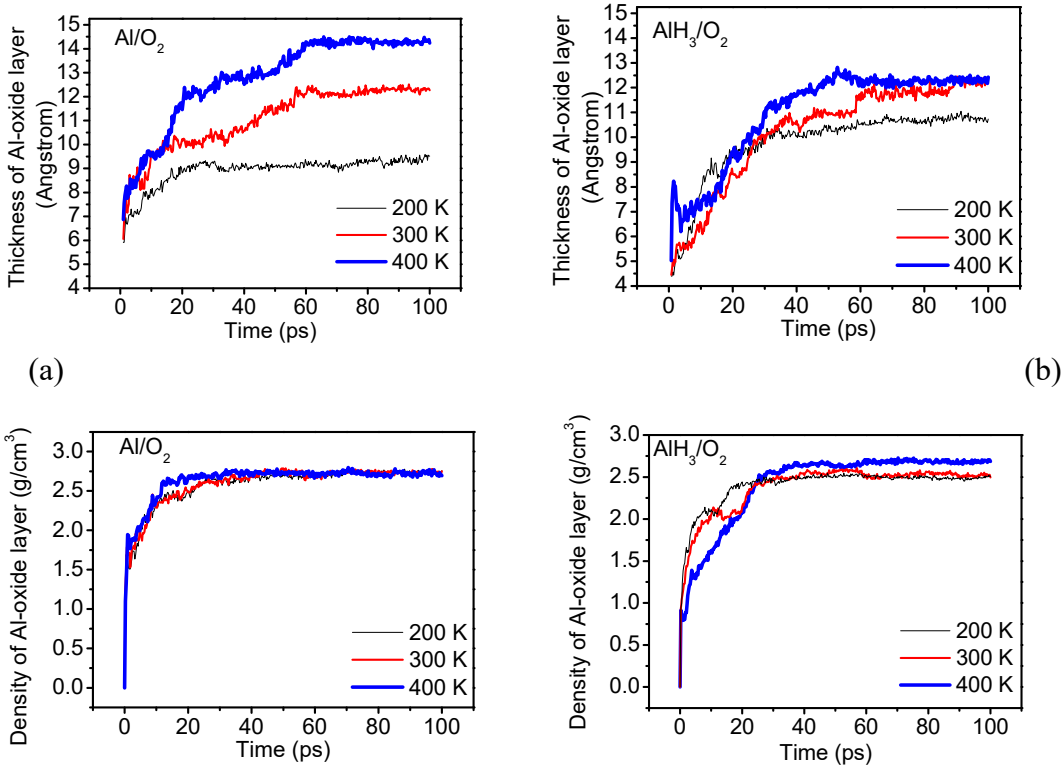
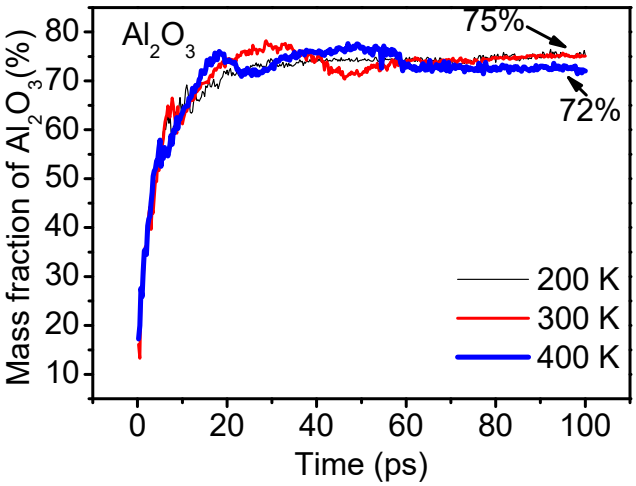


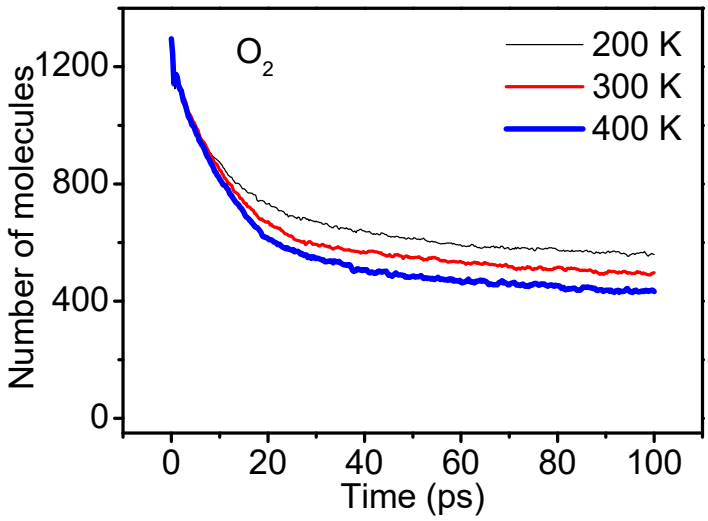
Fig. 2 Changes of thickness and density of passivation layer in Al/O_2 system and AlH_3/O_2 system with time.

3.2 Composition of passivation layer and extraneous gas fragments.

The composition of passivation layer of Al/O_2 system and the content of O_2 outside the layer are shown in Figure 3. The Al_2O_3 content of passivation layer at high temperature is slightly lower than that at low temperature. At the same time, O_2 content decreased slowly at low temperature. The changes of passivation layer composition and extracellular fragments in the AlH_3/O_2 system are shown in Figure 4. At both low and normal temperature, the mass fraction of $Al(OH)_3$ in passivation layer is about 60%, while at high temperature, the content of $Al(OH)_3$ rapidly decreases to about 35%, and the content of Al_2O_3 rapidly increases to about 50%. It shows that during the passivation of AlH3 surface, $Al(OH)_3$ will dehydrate at high temperature and produce more Al_2O_3. This is the reason why the density of the passivation layer on the surface of AlH_3 is larger at high temperatures. At high temperature and normal temperature, the H_2 gas spilled from the surface of AlH_3 will combine with O_2 to form water, while the H_2 content remains unchanged at low temperature.

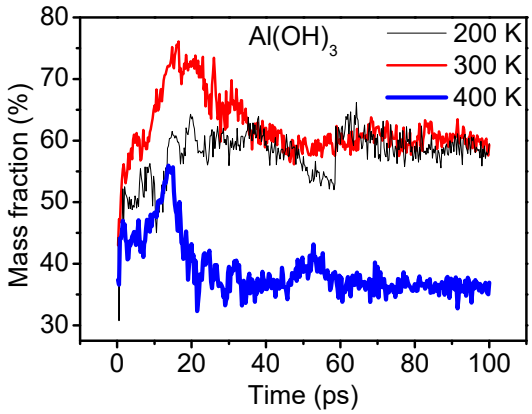


(a)

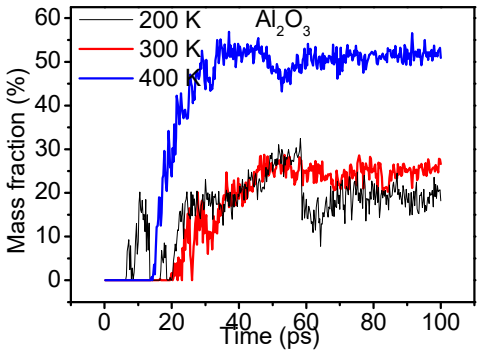


(b)

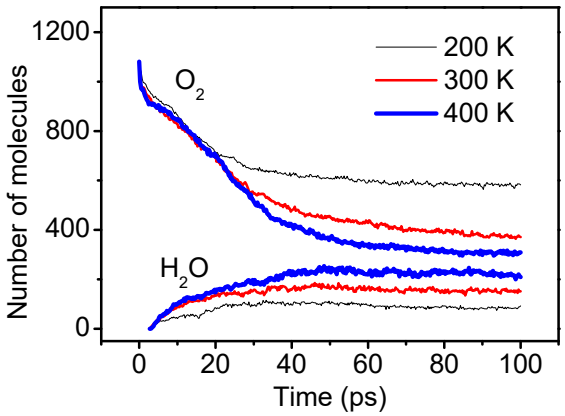
Fig. 3 Changes of passivation layer composition (a) and O_2 (b) outside the layer of Al/O_2 system with time



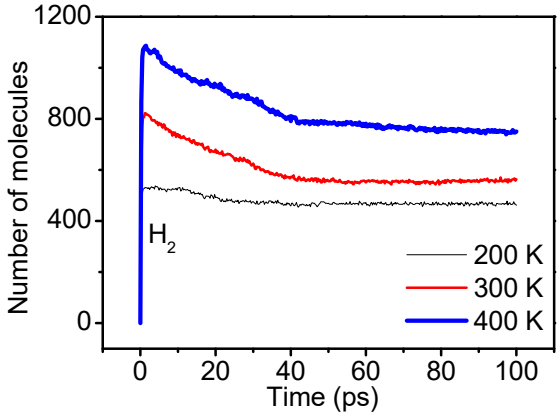
(a)



(b)



(c)



(d)

Fig. 4 The Changes of $Al(OH)_3$ content (a) and Al_2O_3 content (b) in the passivation layer of the AlH_3/O_2 system, and changes of O_2, H_2O (c) and H_2 content (d) outside the layer

4. Conclusion

1. Low temperature can effectively reduce the thickness of the passivation layer on the surface of Al, and slightly increase the Al_2O_3 content in the passivation layer. 2. Low temperature can reduce the thickness of AlH_3 surface passivation layer and increase the content of $Al(OH)_3$ in the layer. 3. At high temperature, $Al(OH)_3$ in the passivation layer on the surface of AlH3 will be dehydrated, forming more Al_2O_3, and increasing the density of the passivation layer.

References

[1] Edgar J H, Gu Z, Taggart K, et al.: Oxidation of aluminum nitride for defect characterization, Kuball M, Myers T H, Redwing J M, Mukai T, editor, Gan, Ain, Inn And Related Materials, Warrendale: Materials Research Soc, 2006: 505-508.

[2] Feng X, Huang Y, Xu H. The Influence of Al on the Detonation Parameters of Aluminized Explosives[J]. Initiators & Pyrotechnics, 2012, (1): 38-41.

[3] Liu Y, Oganov A R, Wang S N, et al. Prediction of new thermodynamically stable aluminum oxides[J]. Scientific Reports, 2015, 5: 6-8.

[4] Wang S, Feng X, Yao L, et al. The Influence of Nanometer Aluminum on the Explosion Heat of RDX-based Explosive[J]. Initiators & Pyrotechnics, 2014, (1): 21-24.

[5] Niu G, Wang S, Jin D, et al. Influence of the Nano-aluminium on Underwater Energy of RDX-based Pressed Explosive[J]. Chinese Journal of Explosives & Propellants, 2015, 38(1): 64-68.

[6] Feng X, Wang X, Xu H, et al. Influence of Al Powder on the Explosion Acceleration Ability for Explosives[J]. Chinese Journal of Explosives & Propellants, 2014, 37(5): 25-28.

[7] Fortes A D, Wood I G, Vocadlo L, et al. Phase behaviour and thermoelastic properties of perdeuterated ammonia hydrate and ice polymorphs from 0 to 2 GPa[J]. Journal Of Applied Crystallography, 2009, 42: 846-866.

[8] Zhurova E A, Zhurov V V, Pinkerton A A. Structure and bonding in beta-HMX-characterization of a trans-annular N---N interaction[J]. Journal Of the American Chemical Society, 2007, 129(45): 13887-13893.

[9] Zhurov V V, Zhurova E A, Stash A I, et al. Importance of the consideration of anharmonic motion in charge-density studies: a comparison of variable-temperature studies on two explosives, RDX and HMX[J]. Acta Crystallographica Section A, 2011, 67: 160-173.