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Reaction characteristics and iron aluminides products analysis of planar interfacial Al/α-Fe_2O_3 nanolaminate

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ABSTRACT

Compared with organic-counterpart or micro-counterpart, nanothermites have attracted substantial interests owing to their exhibited outstanding properties. A common goal of a great amount of studies in nanothermite-based energetic materials is to enhance the reaction properties. Thermite planar geometry structural systems have been the promising structures because they are very tunable to control the alternating layered geometry and thickness of fuel and oxidizer. In this article, the planar interfacial contact Al/Fe_2O_3 nanolaminate thermite systems were studied to explore the effects of variations in preheating temperature, preheating rate and the initial distance between participating fuel and oxidizer on reaction properties and products characterizations by using the classic molecular dynamics simulations. According to the results, ignition delay and reaction time decrease with increasing the preheating temperature. The ignition delay and reaction time decrease from hundreds of picoseconds to a few tens of picoseconds. Additionally, higher heating rate results in higher energized structure, and much more energy was absorbed during heating period leading to a much shorter ignition delay. Reaction will start when the initial distance among reactants is shorter than a certain distance after passing through the ignition delay. Analyses also show the majority number of triangular structure for Fe_2Al clusters and a small amount of tetrahedral structure for Fe_3Al clusters during thermite reaction.

1. Introduction

Energetic materials are a kind of substances with a large amount of chemical energy content. When chemical reaction ignited, it would experience an exothermic reaction to convert their chemical energy into thermal energy with a lot of heat released [1–3]. Nano-scale thermites, also commonly referred as metastable interstitial composites or superthermites [4–6], has been reported to become a hot spot in recent years. These kinds of new energetic materials have attracted great attentions and favor to a large number of researchers in several important fields of application, such as welding, pyrotechnics, propellants and explosives [7,8], due to their outstanding properties of shorter ignition delay time, lower ignition temperature, high energy release when ignited due to the ratio increase of surface to volume, faster propagation speeds, better successful control and adaption of the nano-composites size as well as distribution [7,9,10].

Aluminum has been studied for many years and exhibited the great advantages of high energy density, low cost, adequate resources and low melting temperature. Thus, it was considered to be a primary fuel which integrated into a variety of composite thermites to induce a rapid and high exothermic oxidation-reduction reaction. The most well-known representative thermites are consisting of metallic fuel and metallic oxide. If ignited, a violent chemical reaction with a large amount of heats of reaction and high temperatures will take place. Nanoscale Al containing nanothermites which are highly reactive can achieve higher combustion velocities and sensitivity to detonation, especially the aerogel counterpart [11]. For instance, the combustion speed of fuel/oxidizer nanocomposite has been reported approximately to be 1 km/s that ~1000 times higher than conventional materials, and thermite reaction temperature can reach 3253 K in reaction areas [11,12]. Nano-thermites can also be ignited at lower temperature than micro-thermites, and the ignition delay time are reduced by up to two orders of magnitude. Among these various aluminum based nano-thermites, the most widely investigated are Al/Fe_2O_3, Al/MoO_3, Al/CuO, Al/WO_3, Al/Bi_2O_3, Al/TiO_2 as well as Al/NiO nanothermite systems [13–19]. So far, with the rapid development of

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science and technology, different size and structure of nanostructured thermites have been synthesized experimentally to study the various performances by using variety of synthetic approaches, mainly including sol-gel process [12,20,21], self-assembled [22], physical mixing of Al and oxidizers with nano-scale grain size [13,23], arrested reactive milling [11,24], deposition method [25]. Modern nano-control technology makes it possible to integrate different accurate controlled nanostructure oxidizers into nanothermites, mainly including nanowires [26], nanofilms [27], nanosphers [28], nanorods [29]. The characterizations of both combustion performances and reactive materials properties are indeed of great importance for the reaction process.

According to the great number of available studies, several obvious factors have significant impact on the behavior of thermite reaction on the whole [30–32]. Ignition sensitivity connected with nano scale thermites, ignition delay and ignition temperature, for instance, is an important research object in theoretical and experimental studies. The morphology and distribution of metal fuel and oxidizer are also the significant factors impacted greatly on reaction processes [33,34]. The distribution of particles is too random, which may be responsible for inhibition of self-sustaining processes. An increasing number of studies have been reported to focus on the planar structural nanoscale thermite system which is also commonly referred to as nanolaminates or nanofilm multilayers. The PVD approach can offer the great control of fuel and oxidizer to the alternating layered geometry. Thus, nanolaminate or multilayers structures are very tunable to control the number of layers and the thickness of each layer. Furthermore, they are also promising structures allowing to provide more opportunities for the great control of the fuel/oxidizer interfacial contact quality, contact area, contact density. Reports concluded that the combustion properties are significantly enhanced by improving interface contact [35,36]. Menon et al. [37] have demonstrated a new fabrication approach to perpendicularly embed an array of high-density Fe_2O_3 into the Al thin film for preparing the highly structured Al/Fe_2O_3 nanocomposites. They realized the highly control of size of participating fuel and oxidizer at nanometer scale and high-density Fe_2O_3 nanowire in closely packed arrangement, so that the precise control of fuel and oxidizer reactants can achieve very intimate physical contact for maximum density during reaction. Aurongzeb et al. [38] have reported the layer morphology of multilayer structural system to provide lager planar interfaces among reactants. Marín et al. [39] have proposed the Cu incorporated Al/CuO nanolaminates structure to form an interfacial Al:Cu alloy. The melting temperature of interfacial Al:Cu alloy is much lower than pure Al, which contributes to the enhancement of its reactivity. Ahn et al. [40] designed the nanostructures of energetic particles with various interfacial contact areas between the fuel and oxidizer to study the effect of the interfacial contact on the explosion reactivity. They demonstrated that the higher interfacial contact areas can result in relatively faster burning rate.

In addition, preheating has been reported to significantly enhance the particle reactivity and further evaluate the reaction performance by reducing ignition delay, increasing adiabatic temperature and enthalpy of reaction. Investigation by Zhao et al. [41] demonstrated that burning rate and propagation velocity increased with an increase in the preheating temperature from 20 °C to 130 °C prior to ignition. Birce et al. [42] studied the propagation behavior by preheating thermites from room temperature up to 170 °C and indicated that flam speed dramatically increased with an increasing initial temperature of reactants. The heating rate is also greatly responsible for thermal properties, while the important role of particles size played in thermal behavior of thermites is evident. Michelle and Granier [43] have studied the effect of heating rate on Al/MoO_3 thermite reaction. They varied the heating rate ranging from 2.5 to 15 K min^{-1} and showed the results that the differences in heating rate giving rise to different ignition and reaction mechanism. Investigations by Emily and Michelle [44] on the effect of heating rates on reaction characteristics, showed that ignition delay time are greatly affected by heating rate (decrease with increasing of heating rate), while ignition temperature does not depend on the heating rate.

Many available studies involved nanothermite have confirmedly showed that, the combustion behaviors are considerably enhanced by improving the interfacial physical contact among the reactants. The nanolaminate structural system has been allowed to provide more opportunities for the control of initial interfacial density, contact area. Excellent interfacial contact can result in significant enhancement of explosion reactivity, which would be of great benefit to the interfacial contact quality, contact area and atoms dispersion for pursuing the goal of combustion performance optimization. In the present paper, thus, nanolaminate Al/Fe_2O_3 system with excellent and planar interfacial contact among reactants is our study object to investigate (i) the effect of heating rate and ignition temperature on the nanolaminate Al/Fe_2O_3 thermite reaction; (ii) the effect of variations in the initial distance among reactants on the reaction initiation behaviors; (iii) the activation energy and iron aluminides products during MD heating and thermite reaction reproduction. The simple planar geometry system is also the ideal modeling to attempt to explore its security that sensitivity to initiation of detonation or sensitivity to unwanted initiation of detonation for its important fields of application. Atomic trajectory snapshots are exhibited in order to visually display the behaviors during reaction process. History data of chemical bond breaking and formation, system temperature variation are also given to verify the variety of properties.

2. Classical molecular dynamics (MD) simulations

In this paper, all our calculations are carried out by using the Large-scale Atomic/Molecular Massively Parallel Simulator molecular (LAMMPS) software package [45] and the classical molecular dynamics (MD) simulations with reactive force field, which can mimic the actual reaction processes at the atomic and molecular level. So far, LAMMPS package is still an important tool to increase our understanding of molecular-level behavior since the constitution of sample super-cells can up to several millions, while DFT-MD whose super-cells comprise just approximately several hundred atoms at most, can take several months to finish the calculation. In this paper, we confirmedly choose ReaxFF interatomic potentials presented by van Duin et al. [46] in 2001 at the earliest to describe the bond formation and breaking during the reaction, which is based on the instantaneous bond orders (BOij') to calculate the mainly partial energy contributions to the potential energy. The parameters of reactive force field concerning Al, Fe and O were proposed by Shin et al. [47] in 2012.

The initial configuration of Al/Fe_2O_3 nanoparticles is designed as planar geometry structural for subsequent simulations, just as shown in Fig. 1. The geometric dimensions of Al nanolaminate are respectively set to be 6 nm, 5 nm, and 3 nm. The height and thickness of Fe_2O_3 nanolaminate are set to equal the Al nanoslice 5 nm and 3 nm for conveniently investigate. As to its length, it is set as the numerical value of 4 nm. The simulation structure contains 10,085 atoms in total, including 5425 aluminum atoms, 935 alpha Fe_2O_3 atoms. Non-periodic boundary condition is adopted in all the dynamics simulations. All simulations are performed in the microcanonical (NVE) ensemble with a time-step of 0.2 fs after repeated testing in this work. Therefore, all simulation cases were generally performed with the following three steps.

Thus, (1) a fully equilibrium state structure at 300 K is prepared firstly via the molecular dynamic relaxation for 150 ps. At the first