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Morphological changes of nano-Al agglomerates during reaction and its effect on combustion

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ABSTRACT

Agglomeration of aluminum nanoparticles (nano-Al) is inevitable due to the strong van der Waals forces. It is supposed to affect the combustion characteristics of nano-Al. However, the agglomeration effect is not fully understood yet due to the worse description of the morphological evolution of agglomerates during reaction. In this paper the morphological changes of agglomerated nano-Al, which mainly results from the oxide shell thickening when the particle temperature is below the melting point of alumina, are confirmed in the thermogravimetric analyzer (TGA) and Hencken experiments. Three factors (f_A, f_{ht}, and f_{sp}) are defined to describe the morphological changes quantitatively through proposed formulas. Thus the agglomerate could be equivalent to an effective spherical particle to help studying the effect of agglomeration on combustion. The results indicate two combustion modes for different agglomerates. The small Al agglomerate is hard to combust fully due to the strong heat transfer with ambience, corresponding to the high-temperature oxidation mode. However, at the same environment, as the agglomerate becomes larger, the maximum particle temperature ($T_{p,max}$) increases until that the agglomerate burns fully, corresponding to the fully-fledged combustion mode. At that mode, the burning particle temperature is mainly controlled by the viscous sintering of agglomerates.

1. Introduction

Aluminum nanoparticles (nano-Al), which have high energy density, high reactivity and high adiabatic combustion temperature, could be widely used in many energy applications such as thermites [1], propellants and explosives [2]. Those applications mainly utilize the exothermic reactions through aluminum oxidation/combustion. To understand the reaction mechanisms of nano-Al, lots of experimental and theoretical studies have been conducted, including the investigations of effects of ambient pressure, oxidizer concentration, ambient temperature and particle size [3–6]. Several mechanisms for its reaction have been proposed, such as the ionic diffusion mechanism [7,8], the polymorphic phase transformation mechanism [9] and the melt dispersion mechanism [10]. Although the detailed underlying mechanism is still controversial, the condensed phase reaction is prevalent during the nano-Al combustion [11].

The kinetics of condensed phase reaction of nano-Al could be greatly impacted by the morphologies. Generally, the Al nanoparticles are polydispersed and agglomerated [12,13] due to the strong van der Waals forces. During reaction, the morphologies of Al agglomerates are speculated to change possibly due to the phase transition of the oxide shell [14], the thermal expansion of Al core [10,15] and the physical sintering [13,16]. It is a particularly challenging problem to observe the morphological changes of nanoparticles in-situ under rapid heating and burning conditions, so understanding and description of the real morphological evolutions of burning Al nanoparticles is very insufficient. Recently Sullivan et al. [17] developed a high-heating-rate microscopy to observe the morphological changes of nano-Al and nano-Al/WO_3 after heating pulse. The results indicate that the large morphological changes are possible with a significant heating pulse. Chakraborty and Zachariah [13] discussed the possibility of inter-particle sintering based on the molecular dynamics (MD) simulation. It is found that the characteristic time of inter-particle sintering is comparable to the characteristic reaction time, so the nano-agglomerates could sinter into structures with larger length scales before burning. However, the characteristic sintering time estimated from MD cannot be totally convincing. In the MD simulation, the alumina shell seems behave more like the viscous fluid but not a solidified matter. E.g. the diffusion coefficient from MD simulation ($\sim 10^{-11}$ m^2/s at 1,000 K and 10^{-10} m^2/s at 2,000 K [8]) is a little larger than that derived from viscosity experiment (2×10^{-13} m^2/s at 1,000 K and 10^{-10} m^2/s at 2,000 K [18]) but several orders larger than that derived from the thermogravimetric analyzer (TGA) experiment (10^{-19} m^2/s at 1,000 K, 6×10^{-17} m^2/s at 2,000 K. We derive the

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diffusivities with the similar method of Trunov et al. [9]). The sintering rate is nearly linear with diffusivity. Therefore the estimated sintering time from MD simulation may be several orders smaller than the real one if the alumina is solid. Furthermore, the crystallization of initial amorphous alumina (am-Al_2O_3) shell could take place during combustion [12,17] to impact the sintering mechanism and rate. Yan et al. [19] have given some evidences to support that the initial sintering of aluminum nanopowders is dominated by the grain boundary diffusion. Overall the mechanisms for the morphological change are still not fully understood and need more exploration.

The effects of particle agglomeration on ignition and combustion have been investigated. Mi et al. [20] studied the ignition of boron particle agglomerates and found that the ignition temperature was much lower than that of the single particle. A dual-stage ignition, resulting from the morphological changes during reaction, was confirmed. Shevchuk et al. [21] and Polishchuk et al. [22] constructed an analytical ignition model to analyze the effect of agglomerate size, particle size, density on the ignition temperature, and found a lower ignition temperature for the larger agglomerate. Those investigations could explain some experimental phenomena. However, the morphological changes of agglomerates during reaction are not quantitatively modeled based on physical mechanisms. When modeling the combustion of boron agglomerates, Mi et al. [20] defined a bottleneck width to consider the effect of boron oxide film thickening or thinning on internal gaseous diffusion, but without considering the viscous sintering of molten boron oxide and detailed agglomerate morphologies. As for the combustion of nano-Al agglomerates, related modeling has not been reported yet. The simulation of nano-Al combustion is commonly based on the single particle model [23,24], rarely considering the effect of agglomeration. Therefore, it is of significance to quantify the morphological evolution of Al agglomerates during reaction, thus to help developing a more realistic combustion model of nano-Al agglomerates.

In this article firstly the morphological changes of nano-Al agglomerates during reaction are investigated through TGA and combustion experiments using Hencken burner, combined with the transmission electron microscopy (TEM) analysis. Then different mechanisms are examined through theoretical estimates and morphological comparisons to determine the controlling processes of structural evolution. Thus the morphological evolution of agglomerates is quantified with three factors. Finally the effect of agglomeration on Al combustion is discussed.

2. Experimental method

Al nanoparticles (99.9% pure) from Beijing Dk Nano Technology Co., Ltd are used in the experiment. The primary aluminum particle has a core-shell structure that the aluminum core is covered by an amorphous alumina shell [12]. The number-averaged diameter is about 92 nm by counting the particle sizes from TEM images. Brunauer–Emmet–Teller (BET) surface area and Langmuir surface area of the samples are 14.3 and 19.7 m^2/g, respectively, measured using an ASAP-2020 surface area and porosity analyzer. The corresponding equivalent diameters are estimated to be 107.7 and 78.0 nm, respectively.

Two methods have been applied to treat the nano-Al agglomerates. One method is to let the nano-Al pile in a crucible and oxidize with slow heating rate in the TGA, Netzsch simultaneous thermal analysis (STA) 449F3. The furnace temperature with sample holders has been calibrated using a set of certified pure metals. Samples of 1–3 mg contained in alumina crucibles are heated from room temperature to 1373 K with the heating rate of 30 K/min. The oxidizing environment is a mixture of oxygen and nitrogen with a volume ratio of 17:63. The total gas flow rate is set to 80 mL/min in the experiment. Partially oxidized samples are cooled at around 900 and 1373 K, recovered and analyzed by TEM using JEM2010 (JEOL Ltd.) operating at 120 kV.

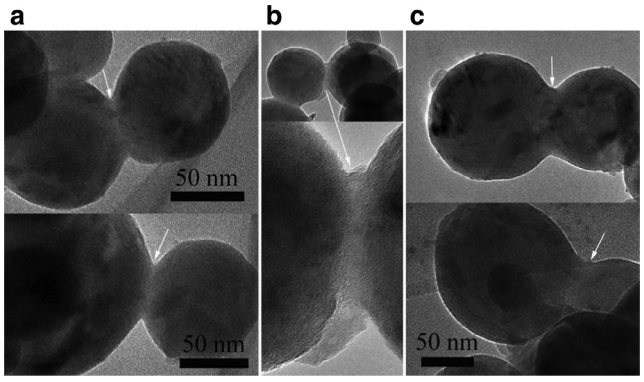

Fig 1. TEM images of contacted particles sampled at around 900 K with heating rate of 30 K/min, (a) Mode One, (b) Mode Two, (c) Mode Three.

The other approach is to burn the airborne nano-Al agglomerates in the post flame region of $CH_4/N_2/O_2$ multi-element, non-premixed flat flames (i.e. Hencken burner), described in detail in a previous publication [12]. The nano-Al is ultrasonically dispersed in ethanol and nebulized to generate small droplets. Those droplets flow through a diffusion dryer, vaporizing to generate small dry airborne agglomerates. Those well dispersed agglomerates are finally fed into the post flame region of the Hencken burner, starting to combust. The products are sampled thermophoretically at different heights above the burner for further off-line analysis by TEM.

3. Morphological changes during reaction

During the TGA experiments with constant heating rate, the conversion of Al increases with temperature. The samples with different reaction conversions at 900 and 1373 K are collected for comparison. Figure 1 shows the TEM images of contacted particles sampled at 900 K in the TGA experiment. Three kinds of contact modes are classified from the TEM images. Mode One (Fig. 1(a)) is a soft connection whose contact neck has a little lighter color in the TEM images, compared with the particle body. Mode Two (Fig. 1(b)) indicates a contact with additional oxide. For those two modes the particles are connected with alumina and the aluminum cores are still separated. However, for Mode Three, the aluminum cores are connected to form a dumbbell shape, as shown in Fig. 1(c). The third contact mode appears possibly due to the initial sintering of aluminum particles during production since this kind of contact is also detected in the original samples (See the supplementary material).

Figure 2 shows TEM images of contacted particles sampled at around 1373 K. At 1373 K, the aluminum is almost totally oxidized. The hollow and crystallized structures can be recognized. In some cases, the hollow cores are connected (Fig. 2(c)) corresponding to Mode Three, while the others are not connected (Fig. 2(a, b)) corresponding to Mode One or Two. A dimensionless contact radius, which is the ratio of the contact radius (R_c) to the radius of smaller contacted particle (R_p), is defined to quantify the degree of densification. The agglomerate is more densified as the dimensionless contact radius becomes larger. In Fig. 1(a), the dimensionless contact radius is around 0.55, while in Fig. 2(b), the dimensionless contact radius increases to around 0.76. It indicates that the agglomerate becomes more densified, as the temperature increases from 900 K to 1373 K.

Figure 3 demonstrates TEM images of samples collected at different heights above the Hencken burner. The corresponding reaction time varies from 0.15 ms to 4 ms. The ambient temperature is 1150 K and the maximum particle temperature could be 300∼400 K higher [12]. As shown in Fig. 3, the primary particles are still distinguishable

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