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Combustion of aluminum nanoparticle agglomerates: From mild oxidation to microexplosion

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Abstract

While the nano-sized energetic materials are featured with ultra-high energy density, the ubiquitous agglomeration in their combustion is still unexplored. In this paper, the combustion characteristics of aluminum nanoparticle agglomerates in the size range of 4–20 μm are investigated on a modified Hencken burner with different temperature (800–1800 K) and oxygen concentration (0.5–5.5 mol/m^3). Due to the heat accumulation effect of the designed porous structures, the nanoparticle agglomerates even maintain the advantages of combustion process of single nanoparticle in terms of a low ignition temperature (~800 K) and a fast energy release rate. Further, the combustion of agglomerates is numerically studied by a newly-developed model, which accurately predicts both burn time and temperature of agglomerate of the mild combustion process. The microexplosion phenomenon occurs when the oxygen concentration exceeds 3.5 mol/m^3. Measurements of particle temperature, burn time, emission spectra and morphologies indicate that this explosion is driven by the vaporization of unreacted aluminum core, which results in huge stresses to tear the Al/Al_2O_3 particle into many smaller, dispersed clusters. Thus a melt/vapor dispersion mechanism (MVDM) based on melt dispersion mechanism is proposed to cover the microexplosion and subsequent accelerated oxidation reactions.

Keywords: Agglomerates; Al nanoparticles; Microexplosion; Melt/vapor dispersion mechanism

1. Introduction

Aluminum (Al) particles have long been used as fuel additives in solid propellants and explosives due to their high energy density (34.2 kJ/cm^3) and low cost [1–3]. Compared with the widely-used conventional Al particles, the nano-sized particles (NPs) with their high surface-to-volume ratio

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exhibit higher reactivity and better performance [4–7].

Due to the high reactivity in nature, Al particles are intrinsically coated with a 2–5 nm thick amorphous alumina shell [8]. The combustion mechanisms of Al NPs depend appreciably on the morphology and integrity of the oxide shell, which is related to the heating rate of the particles. When the heating rate is relatively slow, particles are usually able to maintain their integrity. The oxide shell undergoes a degree of polymorphic phase transition or physical cracking, which provides fast channels for species to diffuse through, thereby resulting in different reaction rate controlling steps [9,10] including the diffusion controlled mechanism and the kinetic controlled mechanism. When the heating is extremely fast ($>10^8$ K/s), the particle may spall, which was described by the melt dispersion mechanism (MDM) [11,12]. The solid shell ruptures when the stress exerted due to the expansion of the melting aluminum core reaches a certain level. The high pressure generates unloading waves and tensile forces to disperse the Al core into a multitude of molten bare clusters. Thus the reaction rate is boosted. For other particles, Badiola and Dreizin [13] reported the microexplosion of micron-sized titanium and zirconium individual particles and attributed it to the release of subsequent nitrogen gas without detailed discussion. However, this kind of microexplosion can only bend the particle streaks [14] but not cause the significant splitting.

The agglomeration of Al NPs is also inherent in practice, where thousands of NPs can be spontaneously connected by Vander Waals forces or Coulomb forces [15]. In one case, Al NPs are reported to be accumulated into micron-sized agglomerates on the surface of propellants before being ignited [16]. Agglomeration also changes the burning characteristics and the morphology of NPs. A positive correlation between burn rate and Al agglomerates size has been indicated for certain composite propellants [17]. For other material (e.g. boron), boron (B) agglomerates were observed to ignite at a temperature that was substantially below the ignition temperature of individual B NPs [18]. A second ignition stage of B agglomerates could be obtained from the rapid evaporation of oxide [19]. With regard to morphology, the primary particles inside the agglomerates sinter faster at high temperatures. The timescale for sintering (< 1 μs) is usually far shorter than the ignition delay ($\sim$100 μs) [20,21]. However, when the agglomerate reaches a certain size, like the NPs in packed form, the alumina shells will rupture after the flash heating [2]. Those different behaviors reveal the transition of reaction mechanisms for agglomerates of different sizes. Small-sized agglomerates can still be regarded as individual NPs and generally described using the conventional models [22,23]. Despite sintering, the burn time was simulated to approach "$d^1 - law$" through correcting the effective diameters, which suggested a heterogeneous kinetics limited mechanism [24]. Nevertheless, ruptured shells of packed NPs provided direct evidence for MDM. Recently, isolated Al NPs generated through de-accumulate dissociation of micron agglomerates showed a fast burn rate [25], which provides another possible reaction path similar to MDM.

The effect of agglomeration on combustion remains controversial. The agglomeration of additives has long been viewed as a purely deleterious phenomenon for longer ignition delays [21], while the porous agglomerates can accumulate the heat within the microstructure and promote morphological changes of agglomerates [19]. Also, agglomeration has the potential to change the reaction mechanisms. The large-sized agglomerates show a mechanism similar to MDM [2], which has not yet been well explained and there is a pressing need to explore the burning behaviors of Al agglomerates. As a first step, the morphological changes of agglomerates were investigated by thermogravimetric analysis in our previous work [26]. Here, the combustion characteristics and mechanisms of micron-sized agglomerates will be further explored and clearly demonstrated, which bridges the gap between the combustion of individual nanoparticles and large particle packings.

In the present work, the combustion behaviors of nanoparticle agglomerates at various temperatures and oxygen concentrations using a Hencken flat-flame burner are investigated by spectral diagnostics and sampling analysis. A combustion model for large agglomerates has been developed to simulate the combustion characteristics and gain more insights into the underlying mechanisms for different oxidation rate. Different reaction modes from mild oxidation to microexplosion have been experimentally observed as the oxygen concentration increase and a novel MVDM (melt/vapor dispersion mechanism) is developed to explain the explosion process.

2. Methodology

2.1. Experimental setup

Fig. 1 shows the schematics of the experimental setup. The apparatus has been used previously to characterize the combustion of well-dispersed Al NPs, where the detailed description was available [27]. A brief summary is presented here. A Hencken burner has been employed to provide a high temperature environment ranging from 700 K to 1900 K. CH_4 and O_2/N_2 mixtures pass through the burner separately to form diffusion flamelets above the honeycomb inside the burner. The post-flame temperature and oxygen concentration are adjusted by changing the flow rate of CH_4, O_2 and N_2. Above the burner along the central line, 17 temperature points at 5 mm intervals are