Brief Communication

Burn time of aluminum nanoparticles: Strong effect of the heating rate and melt-dispersion mechanism

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A R T I C L E   I N F O

A B S T R A C T

A puzzling results were reported for burn time of Al nanoparticles at $T = 1100\,^\circ$C. At a heating rate of 10^3 C/s, the burn time exceeds 1 s [K. Park, D. Lee, A. Rai, D. Mukherjee, M. Zachariah, J. Phys. Chem. B 109 (2005) 7290–7299; M. Zachariah, private communication], while after fast heating (10^7 C/s), the burn time was only 500 µs [T. Bazyn, H. Krier, N. Glumac, Combust. Flame 145 (4) (2006) 703–713; T. Bazyn, H. Krier, N. Glumac, Proc. Combust. Inst. 31 (2007) 2021–2028]. This result is explained by the melt dispersion oxidation mechanism that operates for rapid heating only. Some characteristic parameters of this mechanism (critical heating rate, characteristic cluster size) are estimated.

1. Introduction

It is well known that the particle burn rate decreases with a decrease in particle diameter, which is particularly true for Al particles. Here we discuss two different sets of experimental data for burning of Al nanoparticles with different heating rates but similar conditions otherwise. In the first study [1,2], the heating rate was approximately 10^3 C/s, while in the second one [3,4] it was above 10^7 C/s. Surprisingly, an increase in the heating rate reduced the burn time by four orders of magnitude. We fail to find any reason for such a significant increase in burn rate based on traditional oxidation mechanisms by diffusion of atoms through the growing oxide shell [1,5]. Note that even for a heating rate of 10^8 C/s, the temperature field in nanoparticle is practically homogeneous due to small particle size [6,7]. Recently, a new mechanochemical mechanism (called the melt dispersion mechanism) for fast oxidation of Al nanoparticles covered by a thin alumina shell has been suggested [6–9]. The goal of this letter is two-fold. First, we aim to explain the unexpected effect of the heating rate on the burn rate based on the melt dispersion mechanism. Second, we will use this explanation as a strong and independent support for the melt dispersion mechanism.

2. Experimental results

In reference [1], Al nanoparticles were held for 1 s at $T = 1100\,^\circ$C in air. The estimated heating rate to reach this temperature had an order of magnitude of 10^3 C/s [2]. Such a treatment of Al nanoparticles with diameter $d = 50$ nm covered by an initial alumina shell resulted in only 4% of the particles being completely oxidized [1]. Keeping bare Al nanoparticles with $d = 20$ nm for 1 s at $T = 900\,^\circ$C resulted in 68% of the particles being completely oxidized. Transmission electron microscopy (TEM) in [5] suggests the diffusive oxidation mechanism in which Al and oxygen diffuse toward each other through growing oxide shell. These experimental results are in good correspondence with theoretical modeling [5] of the diffusive oxidation.

In [3,4], Al nanoparticles with $d = 80$ nm covered by an oxide shell were heated behind incident and reflected shock waves in a shock tube. The heating rate can be estimated as follows [10]. For a 80 nm particle heated behind an incident shock, the Nusselt number is approximately 2 (assuming a continuum approach). Since the Biot number is extremely small, the lumped capacitance approach applies. For aluminum particles, this implies a thermal time constant of about 200 ns, which for heating to combustion temperatures yields a heating rate of the order of 10^9 C/s. Taking into account Knudsen number effects will reduce this number by as much as an order of magnitude. Thus, the heating rate was certainly higher than 10^7 C/s and probably reached at least 10^8 C/s. The burn time in a $1100\,^\circ$C was estimated as 500 µs by photometry using 10–90% integrated emission intensity method. Due to a very dilute cloud of particles in the shock tube, interaction between particles is negligible, which corresponds to conditions in [1]. Particle temperatures were measured by optical pyrometer, and the overshoot was typically a few hundred degrees for combustion at pressures near ambient. The burn time decreased with increasing ambient pressure and temperature in a consistent way. Fig. 1 [10] shows a typical emission intensity trace corresponding to combustion of 80 nm Al particles behind an incident shock in air where the temperature is $1227\,^\circ$C and the pressure is 2 atm. The burn time from this plot can be estimated by the full-width

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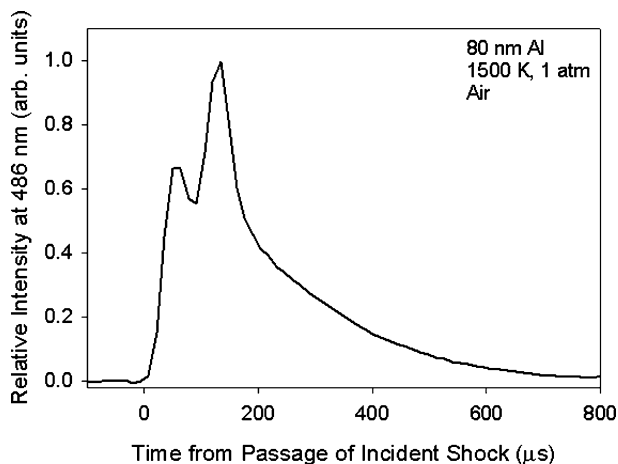 *E-mail address:* vlevitas@iastate.edu.

Fig. 1. Emission intensity trace for 80 nm Al particles behind a 1500 K, 2 atm incident shock in air [10].

Fig. 2. Scheme of the process occurring during fast heating of an aluminum nanoparticle covered by a strong oxide shell and representing a melt-dispersion mechanism. Fast melting of the Al core creates a large internal compressive pressure (one to several GPa) in the Al core and tensile hoop stresses in the alumina shell leading to shell spallation. An unloading wave propagates to the center of Al molten core and generates tensile pressure of the same order of magnitude, which disperses the Al into small clusters.

at half maximum of the intensity plot (<200 µs) or the 10–90% intensity zone (~500 µs). For this plot the emission is collected from the endwall, and so the time for the shock to pass the particle cloud (~100 µs) is convolved in the intensity profile. The actual burn times should be thus ~100 µs shorter than the values listed above. For the conditions of Ref. [1], we can estimate the burn time using the Arrhenius constants from [3], which results in approximately a 50% increase in burn time going from 1100 °C to 1227 °C [10].

Furthermore, detailed analysis of particle size distributions obtained by various techniques on aluminum nanoparticles produced by different methods and suppliers has been conducted in [11,12]. The 80 nm particles studied in [3,4] are produced by NovaCentrix (formerly Nanotechnologies) Inc., Austin, TX, and are similar to particles characterized in [13]. Most powders exhibit a quite broad range of particle sizes. SEM images of the nanopowder with 80 nm mean diameter show some agglomerates with sizes in the range of a few hundred nm, as well as some larger single particles in this size range as well. Since emission intensity during combustion scales with particle mass (d^3), the larger particles have a disproportionate effect on the calculated burn time, and so it is reasonable to conclude that the burn time of the 80 nm particles is significantly less than the measured 500 µs. This assumption is in agreement with the burn time estimated in flame propagation with similar heating rates. Indeed, the order of magnitude of the burn time and the temperature rise time can be estimated based on the measured value of pressure rise time at the reaction front for nano Al and molybdenum trioxide mixture in closed tray experiments, which is ~10 µs [12]. Considering a temperature increase of the order of magnitude of 10^3 K during 10 µs, we arrive at heating rate of the order of magnitude of 10^8 C/s. The pressure in those experiments did not exceed 18 MPa. In open tray experiments [7], when pressure should not deviate from 1 atm, the flame propagation speed was 342 m/s, in comparison with 950 m/s for the closed tray experiment [12], which increased the estimate for burn time proportionally, i.e. to ~30 µs.

The degree of oxidation in shock experiments [3,4] was not measured. However, in similar experiments with the same powder but burning in CO_2 (a much weaker oxidizer), residue collected and analyzed by energy dispersive X-ray spectrometer (EDS) in the TEM showed a ratio of Al:O that was within 7% of stoichiometric, suggesting at least 90% completeness of oxidation [14]. For the more powerful O_2 oxidizer where light emission is much brighter and reaction times faster, it is likely (though not certain) that the degree of oxidation is at least similar. In addition, it is reasonable to assume that such high flame speed as 342 m/s in [7] (in con-
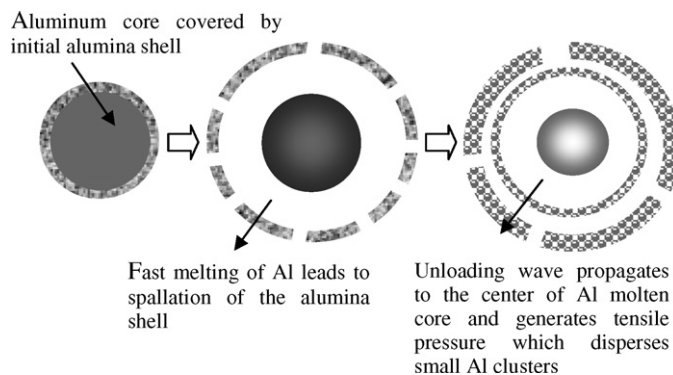
trast to speeds on the order of m/s for micron scale Al particles [15]) can be obtained by complete or almost complete burning of Al nanoparticles. Indeed, unreacted Al serves as a heat absorber and is a deadweight, similar to alumina shell. It reduces the flame temperature and creates barriers for convective flow, thus decreasing flame speed. Since the difference between burn time of 1 s in [1] and 500 µs in [3,4] is so large, the above uncertainties are relatively unimportant. Moreover, the degree of oxidation in [1] is very low (4%) even during 1 s.

3. Melt-dispersion mechanism

The diffusive oxidation mechanism cannot explain a short burn time of 10 to 500 µs observed in experiments reported in [3,4], as well as number of other puzzles discussed in [6,7]. Recently [6–9], we suggested a new mechanochemical mechanism that is not related to diffusion and explains the fast rate of oxidation of Al nanoparticles covered by an initial oxide shell during fast heating (Fig. 2). It is shown theoretically, that the oxide shell for nanoscale particles does not break due to the difference in thermal expansion coefficients of Al and alumina until Al melts. This is in contrast to large micron scale particles for which the oxide shell breaks and heals before Al melting. In fact, the main parameter that determines stresses in a core–shell system according to elasticity theory is not just the Al particle radius, but the ratio of Al core radius R to shell thickness δ, which was confirmed experimentally [8,9]. For $R/\delta < 19$, the entire Al particle melts before oxide fracture [7]. Melting of Al is accompanied by a 6% of volume expansion which creates large pressure (1 to 3 GPa) in the molten Al. Such high pressure overloads the alumina shell with the hoop stresses that exceed the theoretical strength of alumina of ~11 GPa and cause its dynamic spallation.

After oxide spallation, pressure p_0 within molten particle remains the same (several GPa) while at the bare Al surface is $p_f < 10$ MPa due to gas pressure and surface tension [7]. Subsequently, an unloading wave propagates to the center of the particle and creates a tensile pressure of several GPa. Since the tensile pressure exceeds the cavitation limit (strength) of liquid Al, it disperses the Al core into small bare clusters that fly with a high velocity (100–250 m/s) [7]. Oxidation of these clusters is not limited by diffusion through initial oxide shell. The proposed mechanochemical mechanism is called the melt-dispersion mechanism. Various experimental confirmations of the predictions based on the melt-dispersion mechanism can be found in [7–9]. They include quantitative predictions of the flame speed versus R/δ for nano- and