Combustion and Flame 188 (2018) 412–427

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Effect of crystallinity on droplet regression and disruptive burning characteristics of nanofuel droplets containing amorphous and crystalline boron nanoparticles

Pawan Kumar Ojha, Raktim Maji, Srinibas Karmakar*

Department of Aerospace Engineering, Indian Institute of Technology Kharagpur, West Bengal 721302, India

A R T I C L E I N F O

Article history:
Received 20 June 2017
Revised 4 October 2017
Accepted 4 October 2017

Keywords:
Boron
Amorphous
Crystalline
Nanoparticles
Droplet combustion
Agglomerate shell

A B S T R A C T

The present investigation deals with the droplet combustion characteristics of nanofuel droplets containing amorphous and crystalline boron nanoparticles at various particle loadings (0.25%, 1%, 2.5%, 5%, 7.5%, and 10% by weight). Characterization of pre-burnt particles in terms of particle size, morphology, and elemental boron content have been carried out using standard material characterization techniques such as SEM, TEM, XRD and TGA. The droplet burning process has been recorded using a high-speed imaging system. The diameter regression profiles show distinctly different characteristics for amorphous and crystalline particles loaded droplets. Amorphous particles loaded droplets show comparatively smooth regression with minor puffing coupled with shape oscillations at the early stage and micro-explosions at the later stage whereas the crystalline particles loaded droplets show sudden ejections and high-intensity micro-explosions. The morphology of the particle (crystallinity) is considered to be responsible for this difference in burning behaviour. A porous, permeable agglomerate shell forms in case of amorphous boron loaded droplet whereas a densely packed, impermeable agglomerate shell forms in case of crystalline boron loaded droplets during the early stage of burning. The micrographs of post-burning residues indeed reveal that blow holes are present in the agglomerate even at individual particle level for amorphous boron loaded case whereas there are no such blow holes present in crystalline boron loaded case. Thermograms, true colour images of flame and emission spectra show that the amorphous boron particles burn better than their crystalline counterpart.

1. Introduction

The energetic potential of metal or metalloid nanoparticles has driven an interest towards a new class of nanofluid fuels which are recently termed as nanofuels in energy and combustion literature. Nanofuel is a stable colloidal solution in which nanoparticles are suspended in the liquid fuel. It is noteworthy to mention that the nanofuels contain a low concentration of nano-scaled materials which are fundamentally different from the slurry fuels that were studied much earlier [1]. There are many possible contenders as nanoparticle additives for conventional hydrocarbon fuels such as aluminium, beryllium, boron, nickel, magnesium, titanium and zirconium which have been given significant attention because of their positive attributes such as higher specific surface area, higher energy density, potential to reduce ignition delay, and ensuring complete combustion [2]. It is expected that the suspended nanoparticles can act as secondary energy carriers for enhancing energy release from combustion. Of these solid additives, boron is considered as a potential candidate because of its high volumetric and gravimetric energy densities. On complete combustion, boron can provide high energy release hence high combustion chamber temperature and form combustion products with low molecular weight. These exceptional characteristics of boron make it an obvious choice for increasing the performance capabilities in rocket applications [3]. Since the density of boron is around three times of the density of conventional liquid fuels, it can be beneficial for volume limited airbreathing propulsion systems. Though boron has a high energetic potential, the complete combustion of boron is plugged mainly due to two reasons. First, most of the boron nanoparticles contain a native oxide layer on their outer surface which inhibits the ignition process. Second, boron has a very high boiling temperature (~4000 K at 1 atm) whereas the melting temperatures of core boron and its surface oxide (B_2O_3) are 2350 K and 722 K respectively. Due to the lower melting temperature of boron oxide, the molten oxide layer coats the boron surface and hence the combustion process becomes limited by the diffusion

* Corresponding author.
E-mail address: skarmakar@aero.iitkgp.ernet.in (S. Karmakar).

https://doi.org/10.1016/j.combustflame.2017.10.005
0010-2180/

of oxygen/elemental boron through the molten layer [4]. For the realisation of the full energetic potential of boron, the preferred end product is liquid B_2O_3; however, the energy release from the combustion of boron is reduced due to the formation of HBO_2 in a hydrogen containing environment [4]. The reduced energy release due to formation of HBO_2 is sometimes termed as "energy trap" [5,6].

Many early studies on boron combustion are available in the literature [7,8]. One of the pioneering studies was conducted by Macek and Semple [7] in which they first discussed the two-stage combustion processes of boron. The first stage describes the boron particle ignition in which the particle is still coated with an oxide layer. The second stage of boron combustion begins when the particle is heated above the boiling point of B_2O_3 and the oxide layer is completely removed by evaporation. The second stage essentially involves the combustion of bare boron. Therefore, the removal of liquid oxide layer from the particle surface plays a key role in the ignition and combustion of boron [4]. Some researchers have studied the ignition and combustion of dry boron agglomerate and found that the ignition temperature of boron agglomerates is quite lower than the individual particle [9–11]. Mi et al. [11] proposed a dual-stage ignition process for boron agglomerate. The first stage of ignition start at relatively lower temperature compared to individual particle, but the ignition gets quenched when oxygen concentration falls below some critical value. When the oxygen concentration exceeds beyond this critical value, the second stage combustion of boron agglomerates start and it leads to full-fledge combustion. The majority of the previous boron combustion studies involved micron-size particles or dry slurry agglomerates. Only a limited data exist on the combustion of nano-sized boron particles. Particle size plays an important role in ignition and combustion behaviour of energetic particles. It was reported that nanoscale aluminium particles can react at a lower temperature than their micron-sized counterpart [12–14]. Researchers [15] reported that the decrease in particle size of boron can also lower the ignition temperature.

Many experimental studies were conducted earlier to characterise the burning of slurry droplets, mostly involving micron-sized boron [16–18], aluminium [19–21], carbon, and a blend of aluminium and carbon [22–24]. The particle loadings in all these studies were quite high (around 40-80%). A review on various experimental and theoretical studies conducted on slurry fuels is provided by Choudhury [1]. From the thermodynamic point of view, higher loading of energetic particles in liquid (slurry fuel) is always considered to be beneficial. However, slurry fuel has some practical limitations due to significant change in physical properties such as viscosity, surface tension etc. Major problems are rapid settlement of particles, handling characteristics, storage stability, problem in atomization, and longer burning time of agglomerates [1,25–27]. On contrary, the fuel properties of nanofuel do not change significantly due to the low concentration of nanometric materials in nanofuel. Additionally, nanoparticles loaded in the liquid fuel can enhance combustion performance. For instance, a recent study by Xiu-tian-feng E et al. [28] assessed that 12.7% (weight basis) boron NPs dispersed in JP-10 fuel increases the density and volumetric energy from 0.93 g/mL and 39.4 MJ/L to 0.98 g/mL and 43.4 MJ/L respectively. They showed that the dispersed particles were stable for longer period (at least 6 weeks) and the suspension could flow freely like liquid fuel. The viscosity of nanoparticles laden JP-10 was reported to be low at low temperature. Thus, the current fuel delivery systems could still be used without any modification or with little modification [29].

Very limited studies have been performed on the burning characteristics of the liquid fuel loaded with nanoparticles. Tyagi et al. [30] studied the ignition characteristics of a pure liquid fuel (diesel) and diesel with dispersed Al nanoparticles in a simple hot-plate experiment. They found that the ignition probability was significantly higher for the diesel containing aluminium than that of pure diesel. Using a shock tube, Jackson et al. [31] found that the ignition delay time of n-dodecane was substantially reduced with the addition of aluminium nanoparticles above 1175 K. This was further supported by Allen et al. [32] who observed that an addition of 2% (by weight) aluminium nanoparticles in ethanol and JP-8 could reduce the ignition delay by 32.0% and 50% respectively. Saad et al. [33] performed droplet combustion study of pure ethanol and ethanol with aluminium nanoparticles at varying concentrations (up to 5 wt%). Their results showed that the droplet burning rate increased by 140% with the addition of 5% aluminium nanoparticles. Gan et al. [34] performed single droplet combustion study on nanofluid fuel containing boron and iron particles. For dense suspension, it was observed that most of the particles burned as large agglomerate at a later stage of droplet burning when all the liquid fuel had been consumed. However, for dilute suspensions, both the droplet and particles burned simultaneously. Gan et al. [35] carried out a single droplet combustion study on nano-size and micron-size aluminium particles dispersed in ethanol and n-decane. They identified five distinctive stages (preheating and ignition, classical combustion, micro-explosion, surfactant flame, and aluminium droplet flame) for an n-decane/nano-Al droplet, whereas for an n-decane/ micro-Al droplet, only first three stages were observed. They explained that the reason behind this difference could be due to the difference in structure and characteristics of particle agglomerates formed during the early stage of burning. In the case of nano-Al suspension, it is a porous permeable and more uniformly distributed aggregate shell whereas it is densely packed impermeable shell for the micro-Al suspension.

The researchers further suggest that polymorphic phase transitions, crystallinity, particle size and surface morphology play a critical role in ignition and combustion of boron particles [36,37]. Many experimental studies revealed that the burning of crystalline boron is slower compared to amorphous boron [38,39]. These studies were performed on micron-sized boron particles. Takahashi et al. [17] studied the burning of JP-10/boron considering two different size of boron particles (amorphous particles, 0.20–0.32 μm and crystalline particles, 3.57 μm) in the form of slurry droplets and proposed a three-step mechanism, which includes the d^2-law combustion, shell formation, and disruption stages. Their proposition emphasised the combined role of surfactant, and solid particles in formation of agglomerate shell followed by disruption. Gan et al. [35] focused on the effect of the size of aluminium particles (nano versus micron) on the disruption and micro-explosion behaviour of the droplet. However, the role of crystallinity on the formation of agglomerate shell leading to disruptive burning of either slurry or nanofuel droplet has not been explicitly explored in the previous studies. In the present work, two types of boron particles (amorphous and crystalline) have been chosen. The particles with comparable size range have been selected for this study with an idea to address the role of the morphology of boron particles on combustion characteristics of boron/Jet A-1 nanofuel droplet. The motive is to investigate the morphological effect of boron particles in the aggregation process and its effect on the structure, and nature (permeability) of the agglomerate shell formed inside the nanofuel droplet. Additionally, the effect of crystallinity on the particle burning has also been investigated through the analysis of true colour images of the flame and spectroscopic results.

2. Experimental methods

2.1. Fuel preparation

Two types of boron particles, purchased from Sigma-Aldrich and Nanoshel were used in the present study. However, both the