Combustion and Flame 156 (2009) 302–309

Contents lists available at ScienceDirect

Combustion and Flame

www.elsevier.com/locate/combustflame

Enhanced reactivity of nano-B/Al/CuO MIC's

K. Sullivan, G. Young, M.R. Zachariah [*]

Department of Mechanical Engineering and Department of Chemistry and Biochemistry, University of Maryland – College Park, College Park, MD 20740, USA

ARTICLE INFO

Article history:
Received 28 November 2007
Received in revised form 28 April 2008
Accepted 30 September 2008
Available online 27 November 2008

Keywords:
Boron
Aluminum
Thermite
Nanoenergetic

ABSTRACT

Aluminum is traditionally used as the primary fuel in nanocomposite energetic systems due to its abundance and high energy release. However, thermodynamically boron releases more energy on both a mass and volumetric basis. Kinetic limitations can explain why boron rarely achieves its full potential in practical combustion applications, and thus has not replaced aluminum as the primary fuel in energetic systems. In particular, the existence of the naturally formed boron oxide (B_2O_3) shell is believed to play a major role in retarding the reactivity by acting as a liquid barrier if it cannot be efficiently removed. In this paper we demonstrate from constant-volume combustion experiments that nanoboron can be used to enhance the reactivity of nanoaluminum-based Metastable Intermolecular Composites (MICs) when the boron is <50 mol% of the fuel. It was also observed that an enhancement was not achieved when micronboron (700 nm) was used. Thermodynamic calculations showed that the aluminum reaction with CuO was sufficient to raise the temperature above ~ 2350 K in those mixtures which showed an enhancement. This is above both the boiling point of B_2O_3 (2338 K) and the melting point of boron (2350 K). A heat transfer model investigates the heating time of boron for temperatures >2350 K (the region where the enhancement is achieved), and includes three heating times; sensible heating, evaporation of the B_2O_3 oxide shell, and the melting of pure boron. The model predicts the removal of the B_2O_3 oxide shell is fast for both the nano- and micronboron, and thus its removal alone cannot explain why nanoboron leads to enhancement while micronboron does not. The major difference in heating times between the nano- and micronboron is the melting time of the boron, with the micronboron taking a significantly longer time to melt than nanoboron. Since the oxide shell removal time is fast for both the nano- and micronboron, and since the enhancement is only achieved when the primary reaction (Al/CuO) can raise the temperature above 2350 K, we conclude that the melting of boron is also necessary for fast reaction in such formulations. Nanoboron can very quickly be heated relative to micronboron, and on a timescale consistent with the timescale of the Al/CuO reaction, thus allowing it to participate more efficiently in the combustion. The results indicate that sufficiently small boron can enhance the reactivity of a nanoaluminum-based MIC when added as the minor component (<50% by mole) of the fuel.

1. Introduction

Energetic materials consisting of a metal as a fuel and a metal oxide as an oxidizer with particle sizes in the nanometer range are termed Metastable Intermolecular Composites (MICs) and give rise to thermite reactions upon ignition. Such materials have received considerable attention due to their high energy densities and reaction temperatures, and their potential use in explosives, pyrotechnics, and propellants is currently being investigated. Perhaps the single most attractive feature of a MIC is that the reactivity can be tuned through easily-adjustable parameters (i.e. particle size, stoichiometry, etc.) making them prime candidates for a wide range of end-user applications, such as initiators for explosives or enhancers for propellants. Traditionally, aluminum has been used as the fuel in thermites due to a combination of its high energy release and its abundance. However, thermodynamically boron is an attractive alternative since it has higher heating values on both a mass and volumetric basis. Table 1 shows the heating values of some metals which could be potential candidates. Other than beryllium, which is not practical due to its toxicity, boron shows higher heating values than all of the other metals.

When exposed to air, aluminum and boron form an oxide shell around the elemental core of fuel. The shell is typically only a few nanometers thick and, on a supermicron level, is an insignificant amount of the particle mass. However, as the particle size transitions into the nanometer regime, the shell becomes a larger portion of the total mass and can play a critical role in the combustion process. Though the heating values clearly suggest that boron should outperform aluminum, the burning mechanisms of these two materials are speculated to be quite different when one takes into consideration the core–shell structure.

---

[*] Corresponding author.
E-mail address: mrz@umd.edu (M.R. Zachariah).

0010-2180/$ – see front matter
doi:10.1016/j.combustflame.2008.09.011

Table 1
Heating values per mass and volume for various metals.

Metal	ΔH per unit mass (kcal/g)	ΔH per unit volume (kcal/cc)
Boron	−14.12	−33.19
Beryllium	−15.88	−29.38
Aluminum	−7.41	−20.01
Titanium	−4.71	−21.20
Vanadium	−3.64	−21.69
Magnesium	−5.91	−10.28
Nickel	−0.98	−8.72

Different theories have been suggested to explain the burning of an aluminum particle with its elemental core and oxide shell. Initially, Glassman [1,2] proposed that metal combustion is similar to droplet combustion, and therefore a D^2 model could be employed to describe the burn time. He further suggested that the ignition and combustion processes would be governed by the melting and boiling points of the metal and metal oxide. Price [3] suggested two possible mechanisms for the breakdown of the aluminum oxide shell and ignition of aluminum particles. The first mechanism involves the very different melting temperature of aluminum oxide (2327 K) and pure aluminum (930 K). As a result, upon particle heating, the elemental core melts and the molten aluminum expands. This induces thermal stresses in the oxide shell, leading to cracks that expose molten aluminum to the oxidizing species. The other possibility is that the oxide layer undergoes melting itself, which would require much higher temperatures for ignition.

More recently, Trunov et al. [4] studied the effects of phase transformations in the oxide shell upon heating. They used thermogravimetric analysis and X-ray diffraction to study the oxidation of aluminum particles with various sizes and morphologies, and found that aluminum combustion can be explained by a four-stage process. During the first stage, the thickness of the initial amorphous oxide shell increases until it reaches a critical value of about 5 nm. The next stage involves the transformation of the oxide layer into denser γ-Al_2O_3, exposing some of the core aluminum. In the third stage, the γ-Al_2O_3 layer grows and partially transforms into θ-Al_2O_3 and δ-Al_2O_3. Finally, stage four involves the transformation of the shell into stable α-Al_2O_3. In recent work by our group on nanoaluminum, Rai et al. [5] found that aluminum melting was necessary for fast reaction, and was due to the counter diffusion of aluminum metal out rather than oxidizer to the core. This results in the formation under some conditions of a hollow alumina product. Olsen and Beckstead [6] also showed the formation of a hollow product in combustion studies of micron-sized particles.

In boron, a different observation is made during particle heating. Similar to aluminum, a boron particle has an oxide shell (B_2O_3) which surrounds the elemental boron core. The oxide layer, however, melts at a much lower temperature (722 K) than the core (2375 K), rendering a different burning scenario than aluminum. Upon heating, the oxide shell will melt before the solid core, thus leading to a diffusion-controlled process through the molten shell. The pioneering work of Macek and Semple [7] suggested that boron combustion always happens in a two-step process, separated by a dark period. The first step involves the removal of the oxide layer, while the second step involves the burning of a bare boron particle in air. Ulas et al. [8] also support that the combustion of boron particles is defined by a two-stage process. Again, the first stage of boron combustion was considered as the removal of the oxide layer. This process is a slow, kinetic and/or diffusion controlled process, which constitutes a significant portion of the overall burning time of the particle. After removal of the oxide layer, the second stage begins with the combustion of the pure boron.

Contradicting theories about the treatment of diffusion through the molten B_2O_3 layer have been proposed, with Glassman [9] suggesting that elemental boron dissolves into the molten B_2O_3 layer and diffuses outward to the $B_2O_{3(L)}$/gas interface, while King [10–13] suggested that O_2 dissolves into the molten layer and inwards to the $B/B_2O_{3(L)}$ interface. This argument has been more recently addressed in a review article by Yeh and Kuo [14], where they report that the diffusion of boron into the molten $B_2O_{3(L)}$ dominates the diffusion process. They also report the formation of a polymeric vitreous $(BO)_n$ complex in the reaction between dissolved boron and molten B_2O_3. These results were used to develop a reaction mechanism for boron combustion.

Aluminum and boron differ in their combustion mechanisms primarily due to the inherent properties of the pure material and their oxides. Based upon Glassman's Criterion [15], aluminum will combust in a vapor phase in an oxygen environment since its oxide's volatilization temperature is higher than the boiling point of pure aluminum. On the other hand, boron will not combust in the vapor phase since the boiling point of pure boron is significantly higher than the volatilization temperature of its oxide. In fact, since boron oxide melts at a much lower temperature than pure boron, it covers the particle and creates a substantial diffusive barrier between the oxidizer and pure fuel.

Despite the great potential of boron as a fuel, it has rarely achieved its potential in systems that require fast and complete combustion. Ulas et al. [8] suggest there are two major reasons for this; (1) the ignition of boron particles is significantly delayed due to the presence of an oxide layer on the particle surface, and (2) the energy release is during the combustion process of boron particles in hydrogen containing gases is significantly lowered due to the formation of HBO_2. Yetter [16] adds to these issues the idea of an energy trap. Hydrogen containing species can accelerate the gas-phase combustion process. Unfortunately they promote the formation of HBO_2, which is thermodynamically favored over gaseous B_2O_3 as the temperature is lowered, which can result in the boron being "trapped" as HBO_2 and therefore not releasing all of its available energy. The energy trap arises from the fact that from an energetic standpoint, the best product of boron combustion is liquid boron oxide. Even in non-hydrogen containing environments, the quickest way to remove the oxide layer and combust the pure boron material is at temperatures above the B_2O_3 boiling point of 2338 K. However, combustion at these temperatures would result in the formation of $B_2O_3(g)$ whose heat of formation is approximately one third of the liquid form. Furthermore, in early studies Macek [17] showed that boron particles had burn times up to four times longer than similar sized aluminum in similar environments.

Most recently, an effort has been made to address the issue of oxide layer removal. Difluoroamino-based oxidizers have been developed, and have rejuvenated the hopes for boron combustion. With fluorine as an oxidizing agent, an increase in gas-phase combustion products can be realized; a desired effect for energetic materials. Ulas et al. [8] combusted single boron particles in fluorine-containing environments by injecting particles into the post flame region of a multi-diffusion flat-flame burner. Their results show the disappearance of the apparent "two-step" combustion process in the presence of fluorine, along with decreased burning times. This is a major result for boron combustion since the removal of the oxide layer adds significantly to the overall burning time, and if the oxide layer can be removed more efficiently, then boron might be able to be practically used in energetic formulations.

The primary work on boron particle burning has been studied with particle sizes in the micron range, and few works have investigated the use of nanoboron in composite systems. In separate works, Hunt and Pantoya [18] and Park et al. [19] have shown