Ignition delay kinetic model of boron particle based on bidirectional diffusion mechanism

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A B S T R A C T

Ignition delay time of B particles is one of the key factors that influence their burnout ratio in the afterburner. In this study, the micro/nanofabricated slice measurement of a combustion residue particle of B was carried out. By combining the experimental results obtained with previous experimental results, the surface diffusion mechanism of a single B particle was completely verified. Then, an ignition delay kinetic model of B particle was developed using the principles of semiempirical models. By ensuring the initial ignition temperature, the ignition delay of a single B particle can be divided into two stages: (i) heat transfer stage and (ii) low-temperature oxidation stage. The existence of both O_2 diffusion and $(BO)_n$ diffusion (bidirectional diffusion) was confirmed during the low-temperature oxidation stage. Only heat transfer between the B particle and surroundings occurred during the heat transfer stage, whereas both heat transfer and oxidation occurred during the low-temperature oxidation stage. The oxidation involves four global reactions: (i) evaporation of B_2O_3, (ii) diffusion of O_2, (iii) diffusion of $(BO)_n$, and (iv) reaction of H_2O. The final ignition delay time of a B particle is equal to the sum of the lasting times of heat transfer stage and low-temperature oxidation stage. The results of computed ignition delay time obtained by the model are consistent with the previous experimental data under O_2/H_2O atmosphere. According to the prediction of the model, the increase in the initial particle size will prolong the ignition delay time of a B particle. The ignition delay of a small B particle is dominated by the low-temperature oxidation stage, whereas the ignition delay of a large B particle is dominated by the heat transfer stage.

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1. Introduction

Air-breathing oxygen supply systems are used in solid-ducted rockets [1], that can effectively decrease the content of oxidants in the propellant, increase its energy density, and thus improve the specific impulse. Both the gravimetric and volumetric calorific values of B are significantly higher than other common metal fuels such as Al, Mg, and Zr. Thus, they are particularly suitable for use in oxygen-poor propellants [2,3]. However, the ignition and combustion process of B particles is very complex. Heterogeneous reactions occur during the combustion of B, because of its high melting and boiling points (2348 K and 4273 K, respectively [4]). In addition, the complete oxidation product of B, i.e., B_2O_3, has a low melting point (723 K) and high boiling point (2133 K [4]). Once it is covered on the surface of B particles in the form of a liquid film, the contact of inner B particles and outer O_2 will be hindered. Therefore, extensive experimental and theoretical stud-

ies have been conducted to achieve a higher heat output of B in the rocket motor.

Based on combustion theory [5–7], the combustion of a single B particle under oxygen-containing atmosphere will undergo three processes sequentially. First, a B particle is heated from room temperature to the ignition temperature and begins to glow faintly. This process is known as ignition delay. Second, the particle temperature increases until the liquid oxide film is completely removed, and the melting point of B is reached. The particle continues to glow faintly during the removal of liquid oxide layer. However, it may briefly turn dark after the removal is completed (this phenomenon does not occur under certain situations such as under fluorine-containing atmosphere, high turbulent energy flows, or high-temperature and pressure conditions [8–11]). The second process is known as ignition or first-stage combustion. Finally, the bare B particle continually burn and glow brightly until all of them are burnt. This process is known as combustion or second-stage combustion.

Previous theoretical models of B mainly focused on ignition and combustion. These models can be divided into two types according to the difference in modeling principles [12,13]. One type is mech-

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anism models reported by Brown, Zhou, and Yetter et al. [14–18]. They developed the models based on molecular diffusion and elementary reaction analyses. By extensive and detailed calculation and analysis, the trends of reactants, products, and intermediates with time can be obtained. However, since these models are highly complex, lack of relevant experimental data is the most important factor hindering their progress. The other type is semiempirical models reported by King, Williams, Kuo et al. [6–8,19,20]. They simplified the ignition and combustion of B particles with global reactions. Using mass and energy conservation equations, the trends of parameters such as particle size, oxide layer thickness, and temperature with time can be obtained. The principles of semiempirical models are now relatively mature after more than 40 years of development. Both the model development and application are convenient. Thus, the principles of semiempirical models are used in this study.

Other than ignition and combustion, no visible flame light was observed during the ignition delay. Besides, the ignition delay is usually shorter, causing certain inconvenience for research. Therefore, both the related experimental and theoretical studies are lacking, especially theoretical studies. In some studies, ignition delay was even merged into ignition [12,13]. However, as the residence time of B particles in the afterburner is very short, ignition delay time is often one of the key factors that influence the burnout ratio. With the progress in the models of ignition and combustion, researchers gradually started to pay their attention to ignition delay. In Kuo research group, Ulas et al. [21] developed a model for ignition delay. In their model, the ignition delay was regarded as a pure heat transfer process, and both convection and radiation were considered. The ignition delay time was successfully calculated.

Based on the earlier experimental results, in this study, the ignition delay of B is further divided into two stages of different temperature ranges. The first stage is a heat transfer stage, which starts from room temperature and ends at the initial oxidation temperature. The second stage is a low-temperature oxidation stage, which starts from the initial oxidation temperature and ends at the ignition temperature. In addition, the combustion residue particle of B was analyzed using a dual-beam focused ion beam (FIB) micro/nanofabrication slice technology. By combining the analysis results obtained in this study with previous experimental results, the existence of both O_2 diffusion and $(BO)_n$ diffusion (bidirectional diffusion) was confirmed during the low-temperature oxidation stage. Then, an ignition delay kinetic model of B was developed according to the principles of semiempirical models. The model partition results are consistent with the experimental results of Yeh et al. [6]. After verifying its accuracy, the model was used for the partition of the effect of the initial particle size on the ignition delay time of B.

2. Analysis of modeling object

2.1. Partition of ignition delay

The temperature range of B ignition delay spans from room temperature (approximately 300 K, set to T_0) to the ignition temperature (usually between 1550 and 2000 K [22–24], set to T_i). B is stable and nonreactive at T_0, but starts to oxidize before reaching the ignition temperature. The shock tube experimental results of Krier et al. [5] show that before the visible BO_2 spectral signals were detected, the infrared spectral signals of B_2O_3 were detected. The results of thermal analysis [25–27] show that B clearly started to gain weight since ~900 K at atmospheric pressure. One of our earlier studies [28] showed that the oxidation ratio was only 1.4% when B was heated from room temperature to 873 K. However, the oxidation ratio increased to 5.7% when heated to 973 K. Therefore,

there is an initial oxidation temperature T_{io}, hardly any oxidation proceeds below this temperature. When B is heated between T_{io} and T_i, low-temperature oxidation occurs. Related studies [25, 29–31] indicate that the influencing factors of T_{io} not only include the self-characteristics of B such as the initial radius (set to r_0), initial oxide layer thickness (set to x_0), and crystal form, but also external environment parameters such as pressure, temperature, and gas species. Using T_{io}, the ignition delay of a B particle can be divided into a heat transfer stage and low-temperature oxidation stage.

Liquidation of the initial oxide layer will start when B is heated to the melting point of B_2O_3. During the phase transition, the particle temperature remains constant. Commonly, $x_0 \ll r_0$, i.e., the liquidation time is short enough to be ignored relative to the entire ignition delay. Besides, as the Biot number of B, $Bi_B \ll 0.1$ (~0.0165 for particles between 1 and 3 μm [21]), the effect of intraparticle temperature variation can also be ignored.

2.2. Verification of diffusion mechanism

Because of the existence of a surface oxide layer, the diffusion mechanism in ignition delay and ignition are more complex than that in combustion. Previously, researchers once disputed the diffusion mechanism during the ignition of B. In the 1970s, King et al. [19] proposed the famous O_2 diffusion mechanism; they assumed that the outside O_2 will diffuse through the oxide layer to the inner $B–B_2O_3$ surface and react with B during the ignition. This assumption was then opposed by Li and Williams [20] in the 1990s. They proposed that B will first react with B_2O_3 and generate BO; then, BO will diffuse through the oxide layer to the $B_2O_3–O_2$ surface and oxidize. This is known as the B diffusion mechanism. Years later, Yeh et al. [6] improved the B diffusion mechanism by detecting polymer $(BO)_n$ in the surface oxide layer. Their meticulous experimental analysis showed that B diffused into the oxide layer in the form of $(BO)_n$. Therefore, the improved B diffusion mechanism was named as $(BO)_n$ diffusion.

However, the existence of O_2 diffusion was not denied. In another ignition model, Dreizin et al. [32,33] hypothesized that O_2 dissolved in the boron particle until reaching the solubility limit, then the stoichiometric oxide was formed and exhibited strong heat release. Recently, a new bidirectional diffusion mechanism was proposed by Ao et al. [34]. They proposed the existence of two different oxide layer structures on the surface of B. In one structure, only $(BO)_n$ diffusion exists, whereas both O_2 diffusion and $(BO)_n$ diffusion exist in the other structure. However, their experimental evidence is not enough: (i) They did not verify the composition difference between different contrasts, as the difference in contrast may be caused only by thickness difference. (ii) The experimental temperature (773 K) was far lower than the ignition temperature of B, and even lower than the common initial oxidation temperature in thermal analysis experiments. At such a low temperature, the oxidation may not have started yet in some parts of the particle.

We thus had to verify the surface diffusion mechanism of B once more for this study; however, in the temperature range of the low-temperature oxidation stage during ignition delay. Although the reported experimental temperature was higher in the study of Yeh et al. than in Ao et al., it was still lower than the ignition temperature [6,35]. I.e., the experiments of Yeh et al. have already confirmed the existence of $(BO)_n$ diffusion during the ignition delay stage of B. Therefore, if we further confirm the existence of O_2 diffusion, we also confirm the existence of bidirectional diffusion.

Fortunately, this verification has partially been achieved in one of our earlier studies [28], in which we heated B particles (average diameter of 5 μm, amorphous) to different final temperatures. After cooling in an inert atmosphere, the particles were sliced using