Preparation and Combustion Mechanism of Boron-Based High-Energy Fuels

Subjects: Materials Science, Characterization & Testing
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Due to the characteristics of high energy density and a high calorific value, boron has become a high-energy fuel and shows great potential to be a high-performance candidate for propellants. However, the wide applications of boron are still limited by the characteristics of easy oxidization, ignition difficulty, a long combustion duration, and combustion products that readily adhere to the surface and inhibit full combustion. The boron-based energetic materials can be prepared by surface coating, mechanical milling, and ultrasonic mixing methods. The boron-based composites with different additives had different combustion characteristics. The combustion of boron-based energetic materials can be optimized by removing surface oxide layers, providing extra heat, inhibiting the formation of or the rapid removal of the combustion intermediates, and increasing the diffusion rate of oxygen.

Keywords: boron ; combustion ; combustion efficiency ; boron-based composite

1. Introduction

Aerospace aircraft and tactical missiles generally use ramjets or scramjets as the propulsion system to achieve long flight distances and high speeds [1]. At present, the potential performance of ramjets or scramjets in high-speed vehicles has been fully studied and reported [2]. Among all of the reported fuels, boron has a mass calorific value of 58 MJ/kg and a volume calorific value of 131 MJ/L. Some studies showed that boron-based solid propellant had a high burning rate and high atmospheric pressure at high temperature [3], which make boron-based fuels one of the most attractive materials for ramjet fuels and other propellants [4]. Through the mixing of boron with other reagents to prepare compounds, composites or even blended mixtures with improved combustion efficiency of boron-based energetic materials have attracted sustained attention [10].

2. Preparation of Boron-Based Fuels

Until now, the reported preparation methods of boron-based composites mainly include surface coating [11][12], mechanical milling [13][14][15], ultrasonic mixing [16], ultrasonic dispersion [17], high-energy mechanical ball milling [18], cold spraying [19], self-propagating high-temperature synthesis (SHS) [20][21], mechanical mixing [22], and cryomilling [23]. The cryomilling method achieves a relatively high specific surface area compared with the conventional methods. This method also has several advantages compared with room-temperature milling such as the production of small particles without agglomeration and a reduction in the oxidation of powder because the milling process is performed in a nitrogen or argon atmosphere. How to improve the ignition and combustion performance are the major objects for designing the preparation methodology of boron-based composites.

2.1. Boron–Metal-Based Composites

Compared with the bare boron powder, metals, such as Mg, Al, etc. are easily ignited and can combust fully, making them widely used in solid propellants [24]. Metals or alloys are first adopted to improve the boron combustion performance. The typical structure of amorphous boron is a rough surface and an irregular shape, which can make the particles combine together easily through mutual adhesion, forming stable agglomerated clusters without any external adhesive [25]. The B–Mg-based composite materials were prepared by the typical methodology, which is illustrated in the following. Raw materials with smaller and uniform particle size distribution were preferred to ensure the uniform distribution of magnesium and boron in the agglomerated particles. Agglomerated particles were prepared by drying the slurry of micron-sized amorphous boron and magnesium powder in ethyl acetate. The B–Mg material was prepared under a vacuum drying environment of 80 °C for 24–48 h. The obtained materials were tested in a simulated real combustion chamber to achieve optical diagnosis and pressure measurement. A gas-driven probe was used to quench and collect the combustion products, and the internal structure evolution of the agglomerated particles in the combustion process was also
Some refractory metals, such as iron, etc., have also been explored as additives to accelerate boron combustion. The B–Fe based composites can be obtained by high-energy ball milling and surface-coating methods [25]. High-purity iron and amorphous boron powders were selected as raw materials to prepare B–Fe binary composites in a plant ball-milling machine [26]. The B–Fe composites can also be prepared by the thermal decomposition of iron pentacarbonyl [27][28][29][30]. The reaction was carried out in a 250 mL glass round bottom flask with a rubber stopper, and the whole device was assembled and operated in a glove box filled with argon. To prepare the B–Fe composite, 4.75 g boron powder was loaded in the vessel with 80 mL dodecane, a 25 mm Teflon-coated magnetic stirrer (Strider Instruments, Shanghai, China), and 0.5 mL CE-2000 surfactant. The container was rinsed with argon at a rate of 154 mL/min. The exhaust gas was buffered with 400 mL 0.1 M potassium hydroxide solution to capture the decomposition products of the iron pentacarbonyl reaction. The reaction mixture was stirred under argon flow and heated to 110 °C at a rate of 3 °C/min. The temperature was kept constant for one hour to deoxygenate the solution and remove moisture from the powder sample. The temperature was then raised to 190 °C, and 1.5 mL iron pentacarbonyl was slowly introduced into the reaction flask through the diaphragm with a glass syringe. The container was then kept at 190 °C for 2 h for the full decomposition of pentacarbonyl. Finally, the suspension was cooled to ambient temperature and filtered using a Whatman 1003-055 Grade 3 cellulose filter with a diameter of 55 mm (aperture 6 µm) The powder was collected by vacuum filtration. It was then washed and stored in inert hexane atmosphere.

In addition to Fe, transition metals, such as Co, Ni, Hf, and Zr, have also been investigated as additives to improve the combustion characteristics of boron [14]. These metals generally have relatively high boiling points, which can ensure their retention during the combustion procedure of boron particles. Boron powder with a purity of 95% was selected as the raw material to prepare boron–transition metal energetic composites by high-energy mechanical milling [14][31]. The percentage of the transition metal in the composites was 5 wt%. A certain amount of boron and metal additives were mixed in a 500 mL steel cylinder. Then, 20 mL Pharmaco (reagent-grade) hexane was added as the process control agent (PCA). The vial was sealed in a glove box filled with argon. Hardened steel balls (3/8”—9.5 mm) were employed as grinding media. After grinding, the samples were recovered at room temperature and dried in an argon atmosphere. The typical images of the starting boron and the prepared composite materials [14]. The obtained results showed that the boron particles were easily aggregated. Each aggregated cluster contained a number of nano-particles. Agglomeration was also observed in the boron–transition metal composites. Compared with single boron powder, the composites displayed a rounder and denser state. Hf and Zr easily reacted with boron and formed metal borides, which can prolong the ignition delay time.

2.2. Boron–Metal Oxide-Based Composites

Metal oxides can affect the ignition and combustion performance of boron-based thermite. The thermites could be prepared by a facile method. For example, B/nano-NiO thermite composites can be obtained by a simple procedure. First, the nano-Ni(OH)₂ was prepared through the reaction of NiCl₂·6H₂O and NaOH. Then, the prepared nano-Ni(OH)₂ was coated on the surface of boron powder by precipitation [22]. After the pyrolysis of B/nano-Ni(OH)₂, the B/nano-NiO composite was obtained. XRD tests confirmed that two crystals co-existed in the composite, which indicated that the boron powder was in the amorphous state and the nickel oxide was in a crystalline state. NiO has a high specific surface area and relatively low surface free energy, making it easier for boron to release energy and undergo full combustion. Several synthetic methods of B–metal oxide-based composites had been presented [13].

Other methodologies have been developed to prepare B–metal oxide-based composites that contain CuO, Bi₂O₃, and Fe₂O₃ [18][32]. Amorphous B powder with a purity of 99.5% and the metal oxide were first ultrasonically treated for 30 min in ethane. Then, the ethane was evaporated, and the precipitate was passed through a 45 micron sieve to obtain the designed composites. The composite containing MoO₃ and CO₂O₄ was prepared by similar methodology.

2.3. Boron-Metal Fluoride Composites

The combustion of boron usually forms B₂O₃ in the state of high viscosity at high temperature, which easily adheres to the surface of boron particles, which will eventually inhibit the continuous combustion of boron particles. Therefore, how to quickly remove the B₂O₃ formed during combustion becomes the key factor for the continuous combustion of boron particles. Compared with boron oxide, the boron fluoride or fluorine boric oxide that forms during the process of boron combustion were easily from the boron surface. On the basis of thermite theory, it is suggested that the new reaction materials could be designed in which metal fluorides are utilized to substitute the metal oxide to promote the removal of boron combustion products. Metal fluoride-based nano-composites of aluminum, bismuth, and cobalt, etc., were prepared.
by mechanical milling \textsuperscript{[20]}. The starting material was put into a hardened steel grinding bottle in argon atmosphere to prevent oxidation during grinding.

The B–metal fluoride composites can be prepared by adsorption reaction milling \textsuperscript{[20]}. Amorphous boron with a purity of 95%, CoF\textsubscript{2} with a purity of 98%, and BiF\textsubscript{3} with a purity of 99% were selected as raw materials to prepare boron–metal fluorinated composite powders through reaction mechanical milling. The obtained materials were characterized by XRD, which proved the appearance of Co (cubic) and Bi (rhombic) in the energetic materials.

The boron–metal fluoride composite can also be prepared by the co-deposition method \textsuperscript{[25]}. For example, the B–BiF\textsubscript{3} composites were prepared by the co-precipitation of bismuth nitrate pentahydrate with a purity of 98%, sodium fluoride with a purity of 99%, and amorphous boron powder with a purity of 95% in aqueous media. The B–BiF\textsubscript{3} composite was obtained in the solution.

During the combustion procedure of the B–metal fluoride composite, the metal fluoride can produce HF, which can react with the boron oxidant on the surface and form easily evaporated boron fluoride that eventually promotes the ignition and combustion of amorphous boron particles.

### 2.4. Boron–Nano Metal Carbide-Based Composites

Metal carbide-based materials have the advantage of high activity, high combustion heat, a high combustion rate, and high combustion velocity. Under the normal condition, the metal carbide can maintain high stability and decrease the mechanical sensitivity of energetic materials. The metal carbides are usually adopted in the composite of ramjet fuels. The B–nano carbide composites are usually synthesized by mechanical mixing under an argon atmosphere \textsuperscript{[12]}. The high-purity amorphous boron were first mixed with \textit{n}-TiC, \textit{n}-ZrC, and \textit{n}-SiC, separately. Then, the mixtures were ground to ensure the uniformity of the composites. In addition to the metal carbide, other materials such as boron carbide were also adopted to prepare the composites.

### 2.5. Boron–Fluoropolymer-Based Composites

The combustion of boron can be inhibited by the combustion byproducts, which mainly include boron oxides with high viscosity that can prevent continuous combustion. If the boron oxide can be quickly removed from the surface, the combustion of boron can be thoroughly conducted, releasing all combustion heat.

Similar to the combustion characteristics of boron-metal fluoride composites, the combustion of fluoropolymer can also produce HF, which can inhibit the wrapping of boron by the boron oxide and eventually accelerate the combustion of boron-based materials. It was reported that the addition of fluorine accelerated the gasification process of boron oxide, which improved the combustion performance of boron \textsuperscript{[39]}. Compared with metal fluorides, organic fluoropolymers have a better process ability and higher processing safety, which can be employed as formulate additives \textsuperscript{[39]}. The composites of B–PTFE were prepared by a V-type mixer \textsuperscript{[40]}. The boron powder and two kinds of PTFE, namely, 7C and MP-10, were chosen as raw materials. The two materials were uniformly mixed in a V-type mixer and then emulsified thoroughly. The designed materials were obtained after they were fully dried. Similarly, the preparation of the composites of boron with PVDF, Viton, and THV fluoropolymers obtained similar results \textsuperscript{[39]}.

### 2.6. Boron–Oxidant-Based Composites

The stable combustion of boron needs a continuous supply of oxygen. One of the best oxygen sources for the combustion of boron is sufficient oxidant. Oxidant-enwrapped boron has been investigated as an effective propellant for rockets and other equipment. The oxidants are usually coated on the surface of the boron particles.

Surface coating is a common methodology to prepare boron–oxidant-based composites for metal composites. According to the specific coating material, the oxidant coating can increase the specific surface area, enhance the surface reactivity, and improve the compatibility between particles and binders \textsuperscript{[12],[17]}. Two energetic materials, ammonium perchlorate (AP) and nitroguanidine (NQ), are widely utilized as oxidant coating agents \textsuperscript{[13]}. The AP is usually adopted as an inorganic oxidant \textsuperscript{[41]}, which has a higher oxygen content and provides sufficient oxygen to enhance the ignition and combustion of boron. The NQ has good surface compatibility, high stability, superior performance, and slight corrosivity \textsuperscript{[42]}. Both of them can provide oxygen to promote the ignition and combustion of boron particles. The typical procedure for the preparation of boron–oxidants is as follows. (1) Preparation of the saturated solution of the coating oxidant material, (2) adding a certain proportion of B to the saturated solution, (3) ultrasonicate the mixture for a period, and (4) vaporize and dry the turbid liquid at a certain temperature.
3. Combustion Mechanism of Boron-Based Composites

3.1. Boron–Metal-Based Composites

The combustion of boron–metal-based composites is greatly influenced by the chemical characteristics of the metal and amorphous boron. The metal and boron have different chemical activities in an oxidant atmosphere. Therefore, the combustion of the composite is greatly influenced by the components. On the other hand, the combustion of the composite is also influenced by the ratio of the compounds. The combustion performance of the B–Mg composites is determined by the content of Mg in the materials. During the combustion process, with the increase in temperature, the oxide layer on the boron particle surface and Mg in the composite begin melting one after another. With the increasing Mg content and rising temperature, the vaporized Mg will diffuse onto the surface of boron through the gap in the material. However, at the same time, the molten Mg can block the diffusion through the internal gap in the B–Mg composite, which results in an agglomeration of generated gaseous Mg inside the composite and eventually leads to the explosion of the particles. The combustion process is finally completed with smaller particles. The low melting point and high vapor pressure of Mg decrease the ignition temperature and shorten the ignition delay time and average combustion time.

Compared with Mg, Fe can also be easily oxidized to form various oxidants, which can play the role of oxygen donor to promote the oxidation of boron particles in B–Fe composites. The reaction between Fe and gaseous oxidants can replace the heterogeneous reaction between B and gaseous oxidants. On the other hand, the redox reaction between B and FeO can also take place in a condensed state, which inhibits the formation of HOBO gas. The combustion of B in B–Fe composites is also influenced by the purity of boron particles. The increased purity of B can enhance the combustion efficiency.

Compared with iron, heavy metals usually have higher chemical activity, which can easily be ignited and maintain continuous combustion. The B–Hf binary composites have a shorter combustion time than B–Fe composites with the same elemental ratio, which means that the introduction of Hf significantly improve the combustion characteristics of boron. At the same time, it was also observed that the ignition time of B–Hf and B–Zr composites was prolonged, likely because Zr and Hf readily react with B and form their own borides, intermediate products. The formed intermediate usually results in the incomplete combustion of boron. Therefore, the ignition time of B–Hf and B–Zr composites is prolonged. Compared with Hf and Zr, the role of Co and Ni in the improvement of boron-based composite combustion is quite similar to that of Fe, likely because Co and Ni cannot form multiple oxidation states. The boron-based materials can be prepared by mechanical milling accompanied with the modification of particle diameters and surface modification, which can greatly influence the oxidation kinetics of boron powders. Research on the combustion performance of the composites of B–BiF₃, B–CoF₂, B–Bi, and B–Fe revealed that the combustion kinetics changed considerably with the surface modification, particle size, environment, and metal species.

3.2. Boron–Metal Oxide Composites

Metal oxides have been investigated and adopted in practical application as an important component of metal thermites. The metal oxide can react with more active metals and other reducing agents with the release of a large amount of heat. Boron-based thermites form an important branch of thermites. For example, the high combustion performance of NiO-coated B-based thermite has been confirmed. Compared with Mg-PTFE-coated B, the propellant of the B–NiO/Mg-PTFE composite shows enhanced combustion efficiency, a faster combustion rate, and a higher combustion temperature. This is because B–NiO can absorb the heat generated by the meteorological heat flow and condensed phase composition. At the same time, the composite of B–NiO has a higher specific surface and relatively higher surface free energy; therefore, B–NiO can easily react and release a large amount of heat in the combustion procedure.

Metal oxides, such as MgO, Al₂O₃, Bi₂O₃, CeO₂, Fe₂O₃, CuO, and SnO₂, can also dissolve into liquid B₂O₃. With the increase in the surface temperature of B particles, the metal oxide that dissolved into the liquid oxide layer produced mechanical stress at the interface, which broke through the oxide layer and played a positive role in the removal of boron oxide and promoted the combustion of B particles.

Some metal oxides have a relatively high thermal conductivity coefficient, which can enhance the diffusion of oxygen from metal oxides to boron particles. At the same time, the volume density of oxygen in metal oxides is much higher than that of gaseous oxygen. The oxygen can directly contact and diffuse into the core of boron particles, which eventually promotes the combustion of B particles. Bi₂O₃ has higher oxygen ion conductivity, therefore, the boron–Bi₂O₃ composite can be ignited by the minimum ignition input energy with the minimum ignition delay time. CuO, MoO₃, and Co₃O₄ can also improve the combustion efficiency of boron particles.
3.3. Boron–Metal Fluoride Composites

The combustion of boron can form $\text{B}_2\text{O}_3$ and other boron oxides, which are usually in a viscous state at high temperature and easily adhere to the boron matrix. The boron oxide that adheres to boron particles inhibits the diffusion of oxygen to boron and eventually results in the extinction of the combustion flame. During the combustion procedure of boron-based composites, the metal fluoride can react with the organic additives or decompose at high temperature to form HF, which can react with $\text{B}_2\text{O}_3$ and form low viscosity or volatile materials that can easily be removed from the boron surface. The quick removal of high viscosity boron combustion byproducts enhanced the combustion of boron particles, which eventually resulted in the full combustion of boron particles. The ignition temperature of boron-$\text{BiF}_3$ and boron-$\text{CoF}_2$ composites was lower than the melting point of boron oxide, and the ignition temperature of the composite containing acetonitrile-washed B was higher.

3.4. Boron–Nano-Carbide Composites

The combustion of boron-containing propellant can generate carbon dioxide, water vapor, and ammonia, which can break the oxide film on the surface of boron particles [45]. It has been proved that metal carbides can be used as effective components of solid propellants [46]. The combustion of metal carbide can generate solid components and carbon dioxide gas. The solid components, i.e., the metal oxide, act as catalysts for accelerating the oxidation and combustion of boron particles, while carbon dioxide destroys the external oxide layer and expands the contact area between boron and oxygen. Therefore, metal carbides can be adopted as additives to promote boron combustion.

3.5. Boron–Fluoropolymer Composites

The combustion of fluoropolymer produces fluorine species, which can react with oxide film on the boron particles that plays an important role in improving the oxidation and combustion characteristics of boron particles. When fluorine atoms are contained in the composites, the removal rate of boron oxide is obviously increased. During the pyrolysis process, THV (polymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride) produces fluorine-rich alkanes, which greatly enhance the reaction rate of the boron oxide film, which also effectively gasifies the oxide and forms high energy and high temperature in the composites. The combustion reaction activity of the THV composite is greatly enhanced. Compared with Viton, PVDF (polyvinylidene fluoride) also produces a large amount of HF during pyrolysis despite that the reactivity of PVDF with boron oxide is relatively low. The oxidation and combustion characteristics of boron powder can be improved with an increase in the fluorine content of fluoropolymer.

3.6. Boron–Oxidant Composites

To fully utilize the energy of fuels, an oxidant, as an oxygen source for fuels, is usually added according to the oxygen index of the designed fuel. As the most widely adopted oxidant in propellants, AP and NQ have their special characteristics, such as low cost, easy production, high stability, and so on. Propellants containing AP and NQ showed better combustion performance than the fuels without them. Especially in the ignition stage, the elevated temperature promotes the decomposition of AP and NQ, which can further accelerate the ignition and combustion of the fuels. With the acceleration of combustion, the coating agent decomposes and produces gaseous materials, which can destroy the oxide film on the surface of the boron particles. On the other hand, the coating oxidant will also release a large amount of heat and further accelerate the gasification rate of boron oxide. In the stable combustion stage, the generated decomposition products of propellants will react with boron, and the intermediate products further promote the combustion of the boron particles. Therefore, compared with pure boron, the average ignition time and average combustion time of the composite propellant containing oxidant decrease.

References


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