Research paper

Ignition and combustion characteristics of coated and agglomerated boron

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Received: January 18, 2018 Accepted: November 13, 2019

Abstract

Coated boron and agglomerated boron are the most important ingredients of boron-based fuel-rich propellants, and therefore the study concerning the ignition and combustion performance of them could provide helpful information concerning combustion mechanisms and formulation optimization of the propellants. In this study, coated boron and agglomerated boron with different formulation were prepared, and the ignition and combustion performance of them were investigated by the high-power CO_2 laser ignition system equipped with spectrometer and high-speed camera. The experimental results show that the combustion of coated boron and agglomerated boron could be improved by using compound of boron and magnesium (CBM) as raw material; both higher pressure and higher content of magnesium have positive effect on the combustion intensity of the boron particles; the ignition delay time of boron particles increases after the coating and agglomeration processes due to the slow oxidation of boron, and ingredients and pressure have little effect on the ignition delay time of coated boron and agglomerated boron.

Keywords: ignition and combustion performance, coated boron, agglomerated boron, compound of boron and magnesium, amorphous boron

1. Introduction

The heat of combustion of boron is 58.74 $kJ \cdot g^{-1}$ and 137.45 $kJ \cdot cm^{-3}$ respectively which is much higher than that of magnesium and aluminum, and then the energy of solid fuels could be improved by adding boron as additive[1),2)]. However, the combustion of boron needs more oxygen than that of magnesium and aluminum, thus it is a great advantage to employ boron as the fuel of ramjet[3),4)].

Boron-based fuel-rich propellants are the solid propellants with the highest energy at present, and are promising to be the best energy source for the ducted rocket. Elemental boron could be divided into amorphous boron and crystalline boron, and amorphous boron is usually employed as fuel because of the higher reaction activity and lower price. However, amorphous boron cannot be added into the propellants before some processing because the boron oxide coating on the surface of boron particles is incompatible with the binder hydroxyl terminated polybutadiene (HTPB)[5),6)].

Coating amorphous boron with some materials (ammonium perchlorate, LiF, Mg, etc.) compatible with HTPB is the most common way to process amorphous boron, and then the coated boron could be added into the propellants directly[7)−9)]. In addition, the coating materials usually could improve the ignition and combustion performance of boron particles, and then the combustion efficiency of the propellants would increase with coated boron as an ingredient. Amorphous boron with small particle size (a few microns) is usually employed as fuel, considering the short combustion time. Meanwhile, large amounts of oxidizer with small particle size (also a few microns) must be added into propellants to improve the combustion characteristics of propellants, so it is difficult to prepare the propellants containing so much solid material with small particle size. Agglomerated boron with larger particle size is usually prepared by agglomerating the coated boron together with the binder, and then boron-based fuel-rich propellants containing more boron could be prepared easily by adding a certain

Table 1 Formulation of the samples.

Sample NO.	Boron particle	Mg [%]	B [%]	AP [%]	HTPB [%]	Surfactant [%]	Bulk density [g·cm^{-3}]
a	1# coated boron	7.13	81.97	9.90	0	1	0.93
b	1# agglomerated boron	6.63	76.23	9.21	7	0.93	1.26
c	2# coated boron	8.91	80.19	9.90	0	1	0.92
d	2# agglomerated boron	8.28	74.58	9.21	7	0.93	1.25
e	3# agglomerated boron	8.28	74.58	9.21	7	0.93	1.27

amount of agglomerated boron[10].

There are a lot of researches about the ignition and combustion of boron particles and the fruitful achievement provide a lot of helpful information for applying boron as fuels of high energy[11)–13)]. As mentioned above, coated boron and agglomerated boron rather than amorphous boron particles are regarded as the ingredients of boron-based fuel-rich propellants, and the ignition and combustion performance of them may differ from the one of amorphous boron greatly.

In the previous works, thermal reaction characteristics of coated and agglomerated boron were studied by TGA and DSC[1),4)]. The results show that the reaction characteristics of the samples are different from each other, and the thermal reaction reactivity of amorphous boron is higher than that of coated boron and agglomerated boron. In this study, different kinds of boron were ignited in a pressured and windowed combustor, and the ignition and combustion performance were characterized by spectrometer and high-speed camera. The results of this study may provide some helpful information concerning the combustion mechanism and formulation optimization of boron-based fuel-rich propellants.

2. Formulation of the sample

Boron is difficult to ignite and combust compared with the other hydrocarbon or metal fuels, and then magnesium is usually used as a raw material of coated boron and magnesium due to the better ignition and combustion performance. However, the performance of boron may not be improved to the utmost extent by coating magnesium on boron particles or adding magnesium powder into boron powder because of the low contact area of them. The compound of boron and magnesium (CBM) is a new kind of metal fuel which is prepared by ball milling method with amorphous boron and magnesium as raw materials for several hours, and the ignition and combustion performance of boron can be improved effectively because the contact between boron and magnesium in CBM is much closer than that in the mixture. In addition, the specific area of CBM particles is much lower than that of amorphous boron, and then the propellants could be prepared easier when CBM is employed to prepare the coated boron and agglomerated boron.

In this study, two kinds of coated boron were prepared by using CBM as raw material, and AP was used to coat the CBM particles to improve not only the compatibility between the boron particle and binder but also the ignition and combustion performance of boron particles. Three kinds of agglomerated boron were prepared, and 1# and 2 # agglomerated boron were prepared with HTPB of 7 % and the corresponding coated boron of 93 % as raw materials. Different from 1# and 2# agglomerate boron, the boron used in 3# agglomerated boron was the amorphous boron coated by AP first, and then the agglomerated boron was prepared by mixing coated boron with HTPB and magnesium. Therefore, 2# and 3# agglomerated boron (sample *d* and *e* in Table 1) may make a big difference from the aspect of the ignition and combustion performance even if the chemical components is the same. The formulation of the samples is shown in Table 1.

The morphology of the samples was investigated with a scanning electron microscope (TESCAN VEGA 3 LMH), and the images are shown in Figure 1.

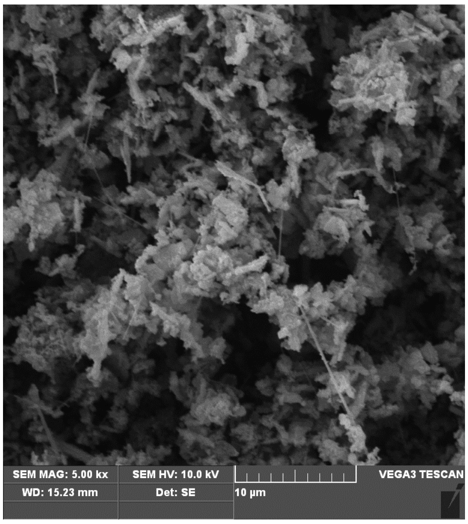
Figure 1 indicates that amorphous boron consists of small irregular boron particles, and the regularity of CBM particles is much better than that of amorphous boron. The small boron particles were held together by AP particles after the coating process, and then the particles size of coated boron is larger than that of amorphous boron. Figure 1 also suggests that most of the agglomerated boron particles are close to spherical in shape, and the average particle size is about 200 μm which will benefit for the increase the content of boron in the propellants.

3. Experiments

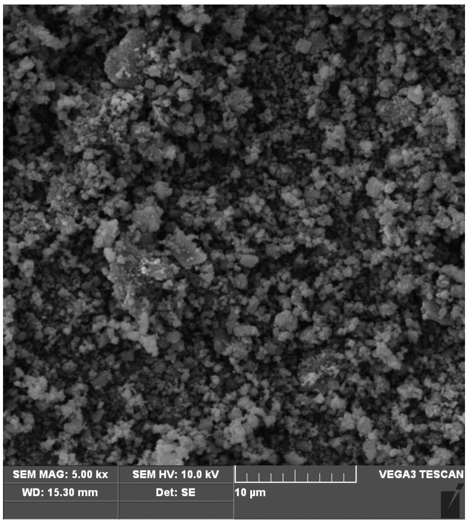
The CO_2 laser with maximum output of 150 W was employed to heat the samples, and the output of 50 W was used in this paper considering the mass and ignition characteristics of the samples. Samples weighting 20 mg were put in an aluminum oxide crucible and ignited in a pressured and windowed combustor. The schematic drawing of the experimental facility is shown in Figure 2[15].

The laser was firstly reflected by a reflector and afterwards focused by a convex lens to heat the samples. In order to study the effect of pressure, the pressure of combustor was set as 0MPa, 0.5 MPa, 1 MPa, and 2 MPa, respectively during the experiment.

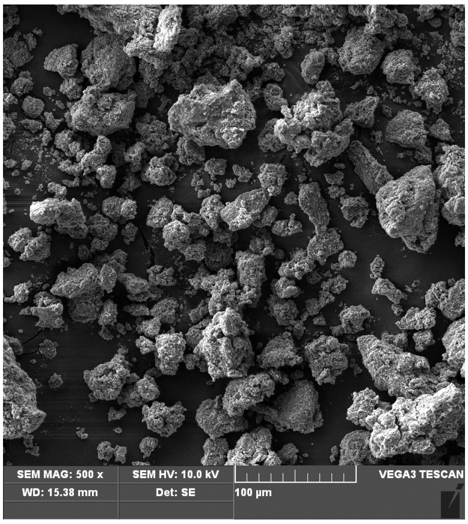
The spectrometer (AvaSpec-2048, Netherlands Avantes BV Co.) and high-speed camera (Phantom V 7.2) were employed to record the ignition and combustion process. In order to get more time-resolved spectrum and photos, the integration time of the spectrum was set as 1.05 ms,



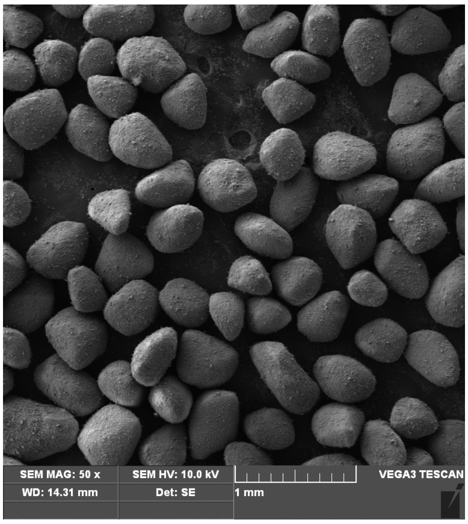
(a) Amorphous boron



(b) CBM



(c) 1# coated boron



(d) 1# agglomerated boron

Figure 1 SEM images of the samples.

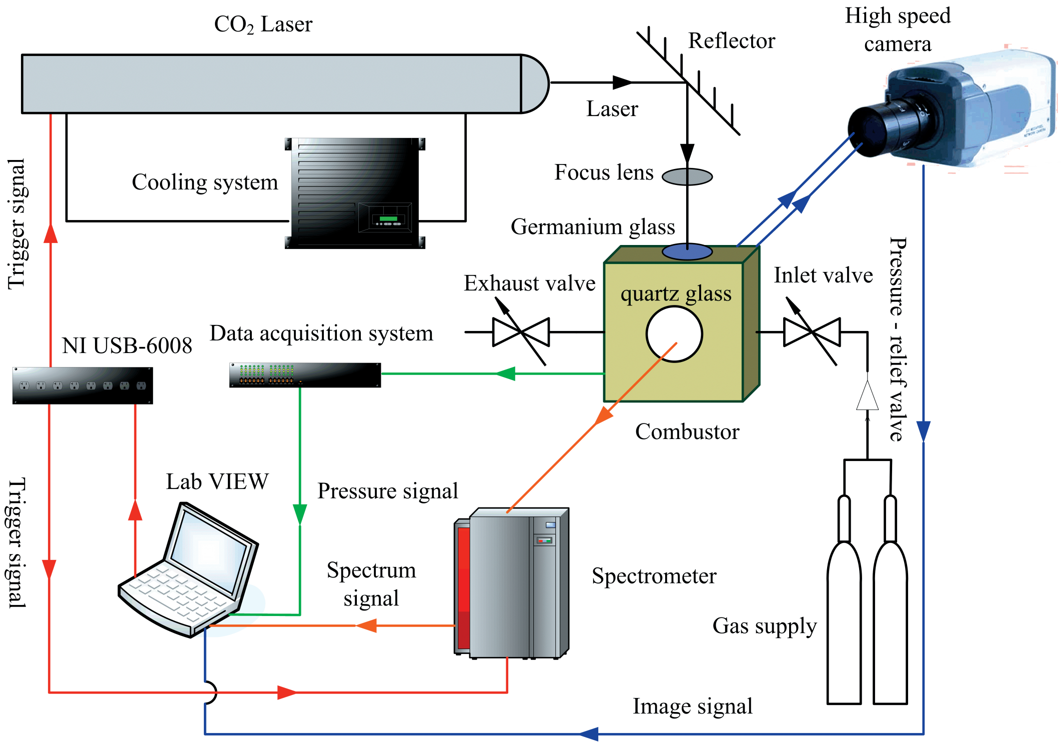


Figure 2 The schematic drawing of the experimental facility.

and the sample rate of the high-speed camera was 5000 fps, so the temporal resolution of spectra and photos during the ignition and combustion processes are 1.05 ms and 0.2 ms, respectively.

4. Results and discussions

4.1 Ignition and combustion process of coated and agglomerated boron

The high-speed camera images during the combustion of amorphous boron (95 % purity), 2# coated boron and 2# agglomerated boron under atmospheric pressure at air atmosphere are shown in Figure 3–5.

It can be seen from Figure 3–5 that there is green flame produced by the emission of BO_2 during the combustion of all the samples. The agglomerated boron burns more violently than the other samples, while the combustion of amorphous boron is the least violent. The combustion of AP and magnesium is much easier than that of boron, and thus the combustion of them would release a lot of energy which favors the combustion of boron; therefore, the burning of amorphous boron is less violent than that of coated boron. The combustion of HTPB could also improve the combustion of boron because of the flammability and heat release during the combustion. In addition, the bulk density of agglomerated boron is much higher than that of coated boron, and then the agglomerated boron generally burns more violently than coated boron.

Figure 6 shows the spectra of three boron particle samples, HTPB and magnesium with the strongest signal during the combustion process.

The strong peaks of 588 nm, 766 nm and 769 nm in Figure 6 and Figure 7 are the interference of sodium, and the other peaks in Figure 6 agree well with the emission of BO_2 that produced by the combustion of boron[16]. Figure 7 indicates that the peaks with high strength for magnesium is located at 371 nm, 383 nm, 499 nm and 516 nm respectively, and there are no obvious peaks for HTPB. As the content of HTPB and magnesium is much lower than that of boron, the spectra in Figure 6 mainly represent the combustion of boron. Figure 6 shows that the combustion of agglomerated boron is the most violent, followed by coated boron and amorphous boron which is consistent with the experimental results of high-speed camera.

The ignition delay time could be used to evaluate the ignition performance of solid fuels, and the ignition delay time of boron particle is usually defined as the time difference between triggering the laser and appearance of the emission of BO_2 in the spectrum because the trigging of the laser and the spectrum are simultaneous. Therefore, the ignition delay time of the samples could be obtained through the analysis of the series of spectra, and the results are shown in Figure 8.

Figure 8 indicates that the ignition delay time of all the coated boron and agglomerated boron is similar with each other and is higher than that of amorphous boron. Therefore, processing methods and ingredients may have little effect on the ignition delay time of the samples.

Figure 3 High-speed camera images of amorphous boron.

Figure 4 High-speed camera images of 2# coated boron.

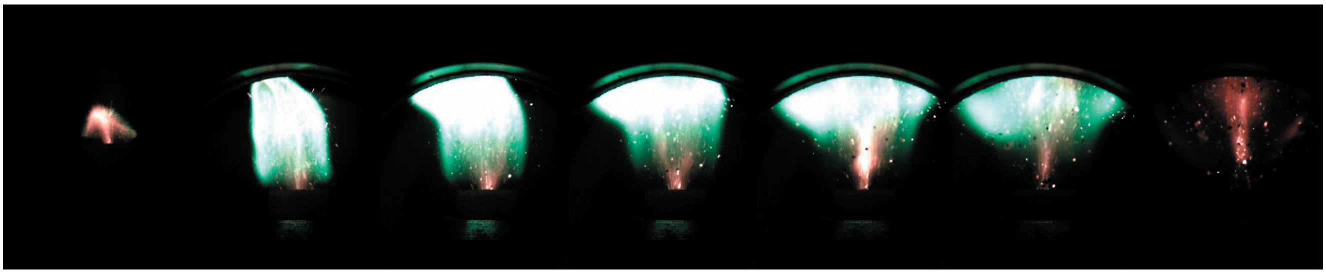


Figure 5 High-speed camera images of 2# agglomerated boron.

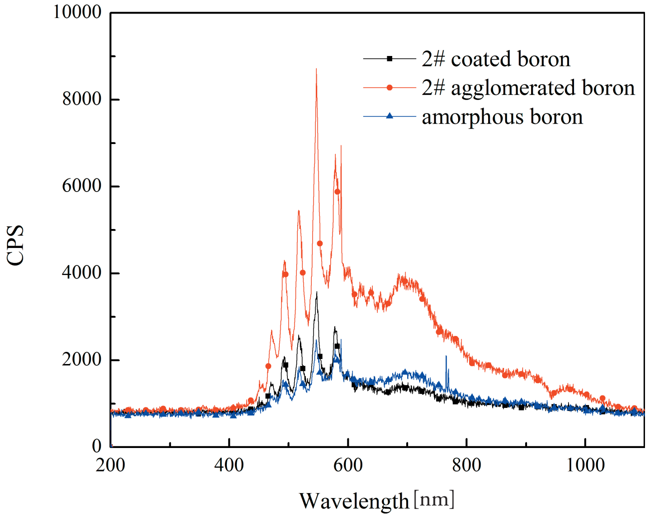


Figure 6 Spectra of the sample under atmospheric pressure.

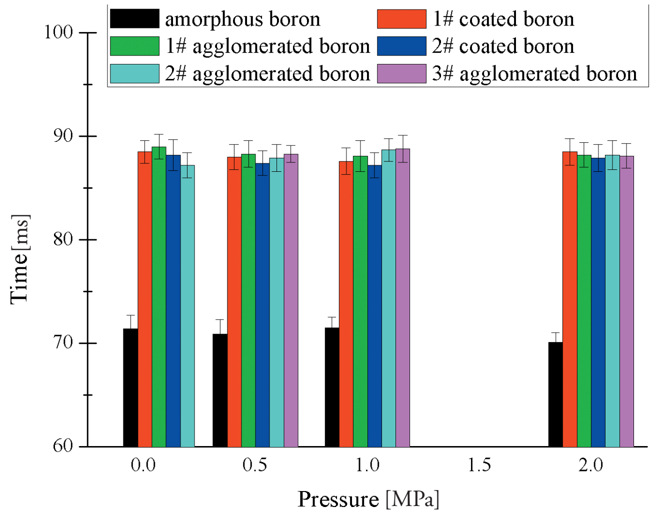


Figure 8 The ignition delay time of the samples.

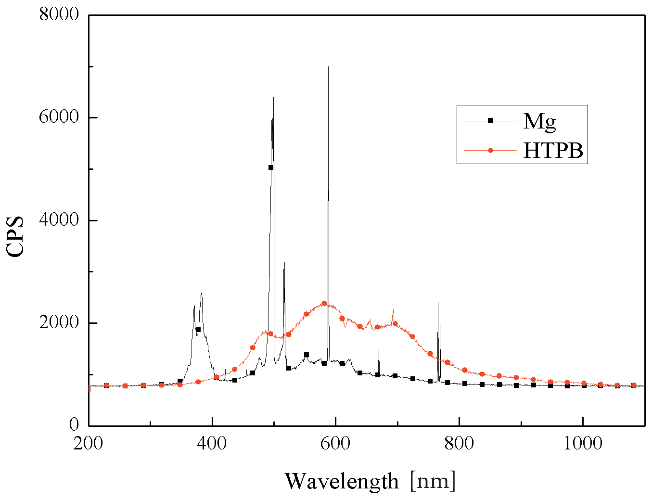


Figure 7 Spectra of HTPB and magnesium under atmospheric pressure.

Amorphous boron is active even at room temperature, and thus could be oxidized by air slowly during the coating and agglomeration processes which would result in the thicker oxide layer on the surface of boron particles. The thicker oxide eventually leads to the longer ignition delay time, however, the oxidation of boron at room temperature essentially completes when the boron oxide film is thick enough for the oxygen to pass through, and then the similar thickness of boron oxide film for the samples leads to the similar ignition delay time.

In addition, it seems that the pressure has little effect on the ignition delay time of the samples. In summary, the ignition delay time of coated boron and agglomerated boron could be regards as a constant (about 88 ms).

4.2 Effect of ingredients on the combustion process

The five samples listed in Table 1 were ignited under atmospheric pressure, and the high-speed camera images and spectra with the strongest signal are shown in Figure 9 and Figure 10.

Figure 9 and Figure 10 show that the strength of spectra is consistent with the brightness and area of the combustion flame represented in the high-speed camera photos. The agglomerated boron burns more violently than the corresponding coated boron mainly because of the higher content of HTPB and higher bulk density. Figure 9 and Figure 10 also indicate that the combustion of 3# agglomerated boron is the least violent. As mentioned above, the contact between boron and magnesium in CBM is much closer than that in the mixture of boron powder and magnesium powder, and then the combustion performance of coated boron and agglomerated boron could be improved by employing CBM as raw material.

Magnesium is much easier to be ignited and the combustion of magnesium release a large amount of heat, and then magnesium is usually employed as the combustion improver of boron. Figure 9 and Figure 10 suggest that the combustion performance of boron improves with the increase of magnesium for both coated boron and agglomerated boron.

4.3 Effect of pressure on the combustion process

High pressure has positive effect on the combustion of boron, and there are some researches concerning the ignition and combustion of boron under high pressure. The shape of spectra during the combustion process of all the samples are almost the same with each other except for the strength. The peak of the spectrum with the strongest signal is located at 547 nm during the combustion of boron, and then the violence of the combustion could be characterized semi-quantitatively by the strength of this peak. Figure 11 represents the strength of the peaks during the combustion of coated boron and agglomerated boron under different pressures.

Figure 11 indicates that the combustion is more violent for all the samples under higher pressure, and the effect of pressure is more efficient under low pressure for coated boron, while more efficient for agglomerated boron under high pressure. The agglomeration of boron particles usually occurs during the combustion process, and it goes further under higher temperature. The coated boron contains AP and boron, both of them combust more violently under higher pressure which will result in more serious agglomeration of boron. Therefore, the

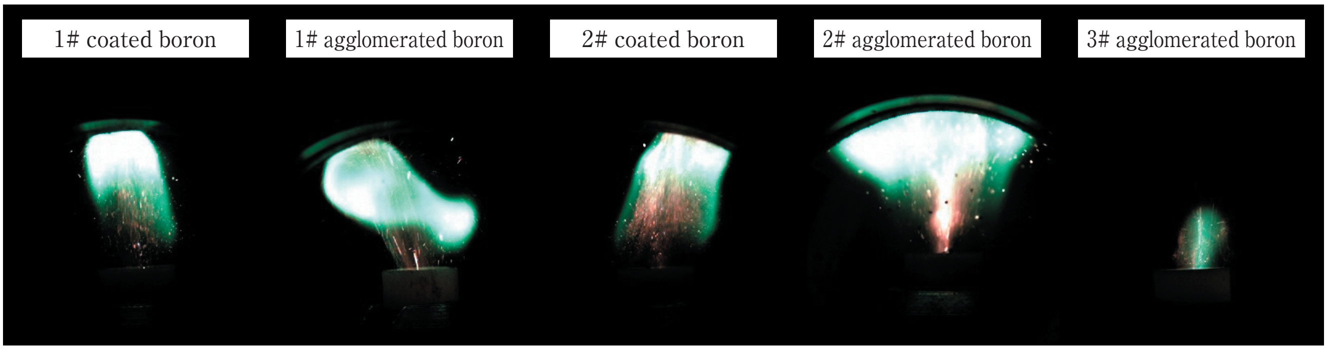


Figure 9 High speed camera images of the samples.

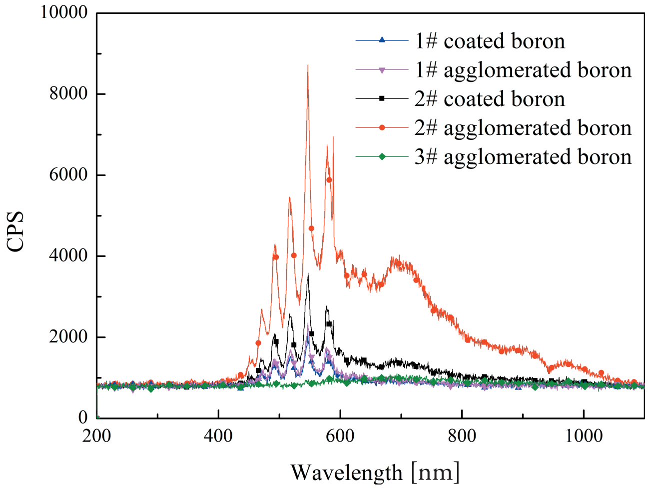


Figure 10 Spectra of coated boron and agglomerated boron.

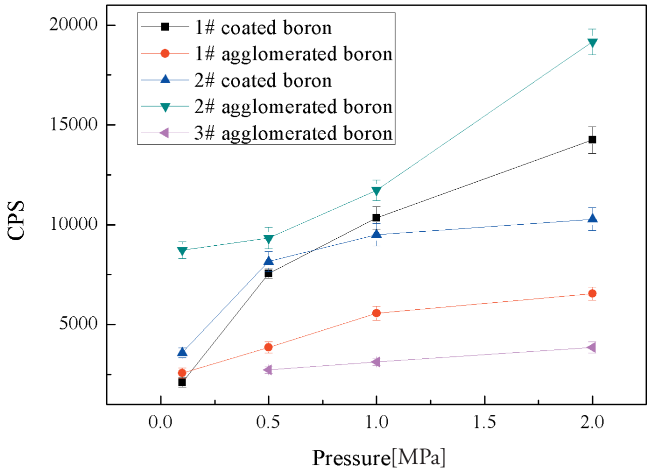


Figure 11 The strength of peaks at 547 nm.

improvement of pressure on the combustion violence could be partly offset by the more serious agglomeration.

Different from the coated boron, there is HTPB in the agglomerated boron, and the combustion of HTPB and AP generates more gaseous products which could improve the agglomeration of boron. The combustion of HTPB and AP was more violent under higher pressure which would make the gas generation rate much higher, and then the combustion violence of agglomerated boron increased more obviously under higher pressure.

Figure 12 shows the high-speed camera photos of the samples combusting under 2 MPa at air atmosphere.

Figure 9 and Figure 12 also suggest that the combustion of all the samples is more violent under higher pressure, and is consistent with the results of spectra. The combustion of 3# agglomerated boron is also the least violent, and again proves the combustion improvement by using CBM as the raw material.

4.4 Effect of ingredients and pressure on the combustion time

Boron usually has low combustion efficiency, and then the samples with higher combustion efficiency would be the preferable raw material of the propellants. The combustion efficiency of boron could generally be obtained through the chemical analysis of combustion products or the mass increase after the combustion. However, some of the products may lose because of the splash during the combustion process, and then the combustion efficiency could not be obtained by the two methods mentioned above. Combustion time is another important parameter that could characterize the combustion efficiency of boron. The combustion time of the samples could be determined by the series of high-speed camera photos in this study, and the results are shown in Figure 13.

The combustion time of boron particles increases with particle size, and generally follow d^2 law for the larger particles due to the diffusion-controlled combustion. However, the combustion time of the samples does not follow this law. The combustion time of single boron particles usually has negative correlation with pressure essentially because of the positive correlation of the reaction rate with pressure, but it can be seen from Figure 13 that the combustion time increases with the pressure for all the samples. In this study, particle clouds were used in the ignition and combustion experiments, and then the combustion time laws may be different from the single particle. Considering that the raw elemental boron particles are similar for all the samples, the longer combustion time indicates the higher combustion efficiency.

Figure 13 also indicates that agglomerated boron has longer combustion time than the corresponding coated boron. Compared with coated boron, there is HTPB in agglomerated boron, and the combustion of HTPB could also releases energy which is in favor of the combustion of boron. Therefore, the combustion efficiency of agglomerated boron may be higher than that of the

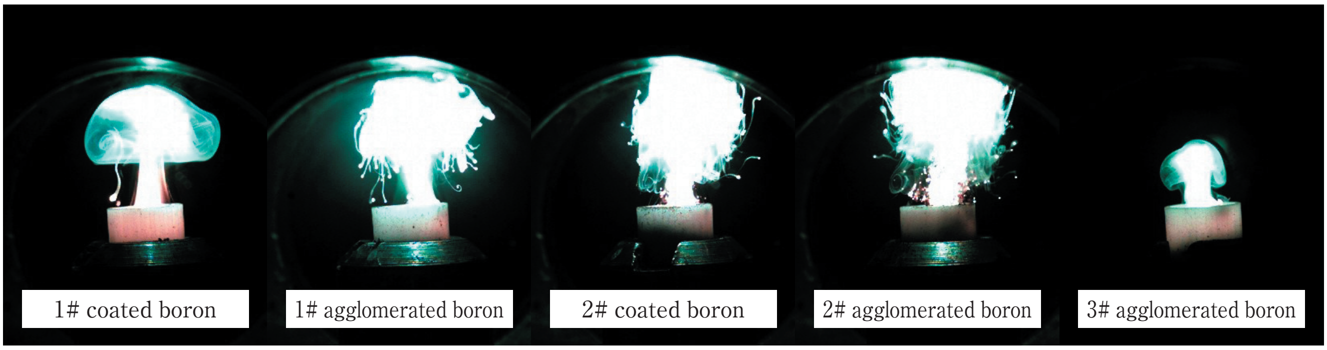


Figure 12 The combustion photos under 2 MPa at air atmosphere.

corresponding coated boron. It can be seen from Figure 11 and Figure 13 that both the combustion violence and the combustion time are the lowest for 3# agglomerated boron, this also indicates that CBM is an ideal raw material of coated boron and agglomerated boron.

In addition, there is more magnesium in 2# coated boron and 2# agglomerated boron, and then the higher content of magnesium would increase not only the combustion violence but also the combustion time of boron which benefit for the combustion efficiency of boron. So boron-based fuel-rich propellants would have better combustion performance by using 2# coated boron and 2# agglomerated boron as raw materials.

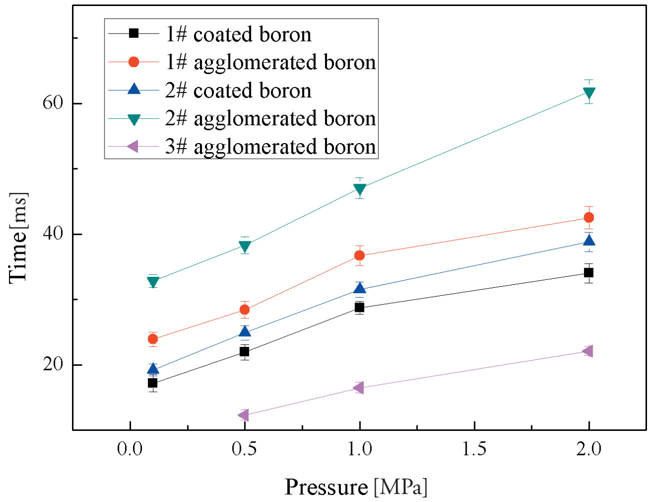


Figure 13 Combustion time of the samples.

5. Conclusions

(1) Compound of boron and magnesium (CBM) could be regarded as a preferable raw material of coated boron and agglomerated boron concerning the high combustion violence and long combustion time, and both combustion violence and combustion time generally increase with the content of magnesium.

(2) Higher pressure has positive effect on the combustion of coated boron and agglomerated boron. The effect of pressure on coated boron is more obvious under low pressure, however, is more obvious for agglomerated boron under high pressure.

(3) The ignition delay time of boron increases after the coating and agglomeration processes because of the slow oxidation of boron at room temperature. It seems that ingredients and pressure have little effect on the ignition delay time of the coated boron and agglomerated boron.

References

1) A. Gany and Y. M. Timnat, Acta Astronaut., 29, 181–187 (1993).
2) H. L. Besser and R. Strecker, Int. J. Energ. Mater. Chem. Propul., 2, 133–178 (1991).
3) E. Buchner and G. Langel, Zeitschrift für Flugwissenschaften., 24, 275–278 (1976).
4) R. S. Fry, J. Propul. Power., 20, 27–58 (2004).
5) W. Q. Pang, X. Z. Fan, W. Zhang, H. X. Xu, J. Z. Li, Y. H. Li, X. B. Shi, and Y. Li, Pyrotechs., 36, 360–366 (2011).
6) Y. H. Wang, B. X. Li, and H. Cai, "Theory and Practice of Energetic Materials", Science Press, (2003). (in Chinese).
7) I. M. Shyu and T. K. Liu, Combust. Flame., 100, 634–644 (1995).
8) T. K. Liu, S. P. Luh, and H. C. Perng, Propellants Explos. Pyrotechs., 16, 156–166 (1991).
9) T.-K. Liu, I.-M. Shyu, and Y.-S. Hsia, J. Propul. Power., 12, 26–33 (1996).
10) L. T. Deluca, E. Marchesi, M. Spreafico, A. Reina, F. Maggi, L. Rossettini, A. Bandera, G. Colombo, and B. M. Kosowski, Int. J. Energ. Mater. Chem. Propul., 9, 9 (2010).
11) C. L. Yeh and K. K. Kuo, Prog. Energ. Combust., 22, 511–541 (1996).
12) R. O. Foelsche, R. L. Burton, and H. Krier, Combust. Flame., 117, 32–58 (1999).
13) W. Ao, W. Yang, Y. Wang, J. Zhou, J. Liu, and K. Cen, J. Propul. Power., 30, 760–764 (2014).
14) L.-l. Liu, G.-q. He, and Y.-h. Wang, J. Therm. Anal. Calorim., 114, 1057–1068 (2013).
15) L. L. Liu, G. Q. He, Y. H. Wang, and S. Q. Hu, Cent. Eur. J. Energ. Mater., 14, 448–460 (2017).
16) M. J. Spalding, H. Krier, and R. L. Burton, Combust. Flame., 120, 200–210 (2000).