



## **Ignition and Combustion Performance of the Primary Condensed-phase Combustion Products from Boron-based Fuel-rich Propellants**

**Lin-lin Liu,\* Guo-qiang He, Ying-hong Wang, Song-qi Hu**

*Science and Technology on Combustion, Internal Flow and Thermal-Structure Laboratory, Northwestern Polytechnical University, Xi'an 710072, P. R. China*

*\*E-mail: viola7788521@163.com*

**Abstract:** The primary condensed-phase combustion products of a boron-based fuel-rich propellant were ignited using a high-power CO<sub>2</sub> laser in a pressurized and windowed combustion chamber under variable pressure. The ignition and combustion performances were characterized using an ultraviolet-visible spectrometer and a high-speed camera. The experimental results showed that the combustion of the condensed-phase combustion products originate from the combustion of carbon, and boron may not take any part in the combustion process because of the formation of a thick boron oxide coating and agglomeration after the primary combustion process. Both particle size and the ingredients play an important role in the combustion reaction of the condensed-phase products. It was observed that a lower particle size and a higher boron carbide content are beneficial for the combustion reaction of the products; higher primary and secondary combustion pressures clearly improved the secondary combustion efficiency of the propellant in the combustion reaction.

**Keywords:** boron-based fuel-rich propellant, primary combustion products, ignition, combustion performance

### **1 Introduction**

Boron-based fuel-rich propellants are regarded as the most promising energy source for solid ducted rockets because of their high energy (> 35 kJ/g) [1-3]. The combustion of boron-based fuel-rich propellants in ducted rockets can be divided

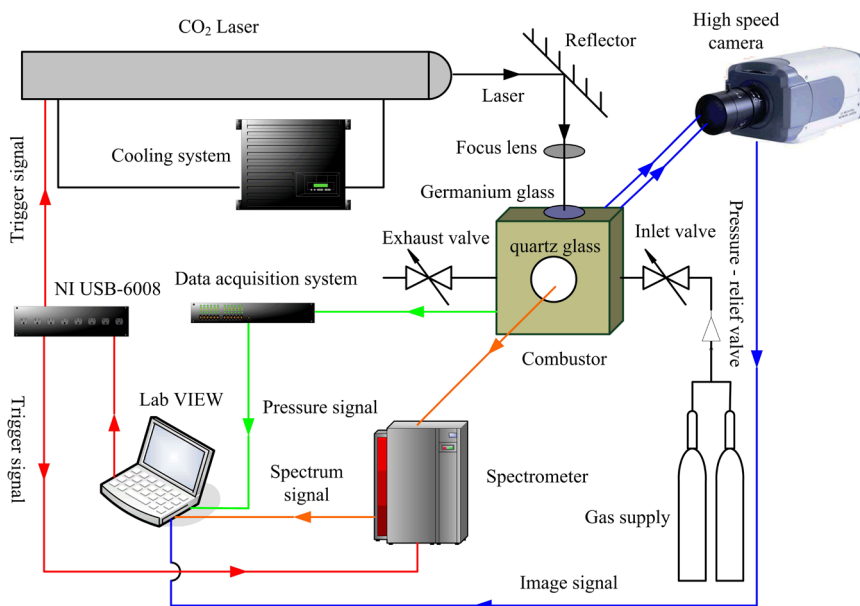
into primary and secondary combustion processes: the primary combustion process occurs in the gas generator, producing the primary combustion products; the secondary combustion process occurs in the ramjet combustor using the primary combustion products and inhaled air as the fuel and oxidizer. Because the oxidizer content in the propellants is much lower, the secondary combustion process releases much more energy than the primary combustion process. Therefore, the secondary combustion process is vital for the performance of solid ducted rockets [4, 5].

The primary combustion products are the fuels for the secondary combustion, and the condensed-phase products, especially boron carbide and boron nitride, are crucial because of difficulty in the ignition and combustion. As reported previously [6], we designed a facility to collect all of the primary combustion products (including the condensed and gaseous-phase products) of boron-based fuel-rich propellants under different operating pressures, and the composition of the primary combustion products and particle-size distribution of the condensed-phase products were determined. The results of this study showed that the composition and particle size of the condensed-phase products vary with the operating pressure, and a large amount of boron carbide may be present in the products.

Although boron carbide can provide almost the same energy as boron [7, 8], it is much more difficult to become oxidized because of its excellent chemical and thermal stabilities [9]. To evaluate the secondary combustion process of boron-based fuel-rich propellants, different primary combustion products were ignited using a CO<sub>2</sub> laser igniter, and the results provide useful information for optimizing the propellant formulation and for determining the influence of the primary combustion conditions on the secondary combustion process.

## 2 Laser Ignition Experiments

A high-power CO<sub>2</sub> laser is often used as a heat source to study the ignition and combustion of boron particles [10, 11]. In the present paper, a CO<sub>2</sub> laser with a maximum output of 150 W was used to heat the samples placed in aluminum oxide crucibles and ignited in a pressurized and windowed combustion chamber. A schematic drawing of the experimental facility is shown in Figure 1.

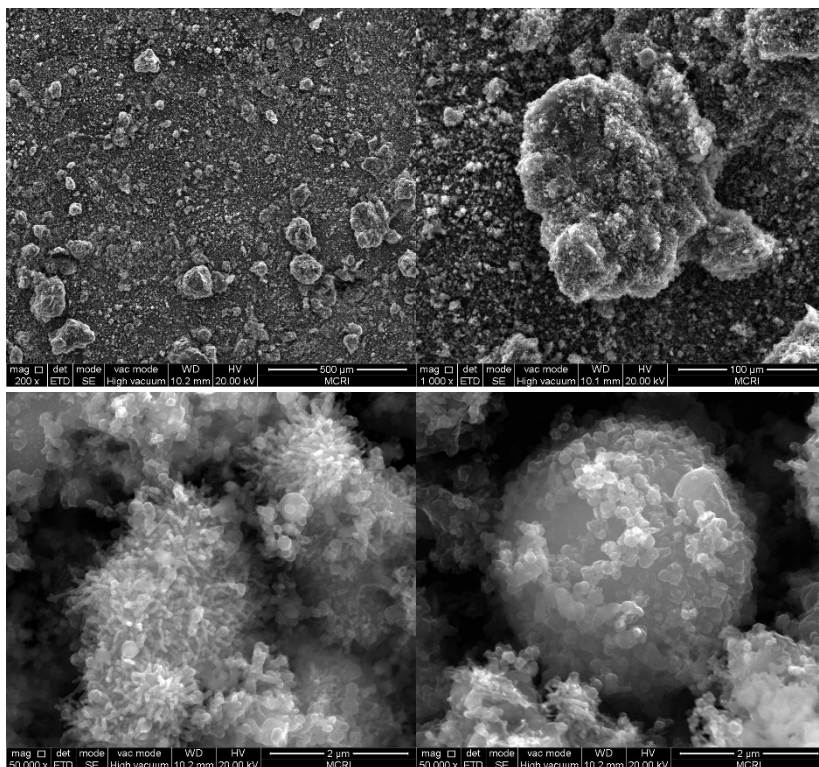


**Figure 1.** Schematic drawing of the experimental facility

Approximately 20 mg samples were used in the experiments, and the pressure was set at 0 MPa, 0.5 MPa, 1 MPa, and 2 MPa. An ultraviolet-visible spectrometer (Avantes AvaSpec-2048) and high-speed camera (Phantom V 7.2) were used to record the ignition and combustion of the samples. To obtain time-resolved spectra and photographs, the integration time of the spectra was set as 1.05 ms, and the image interval of the high-speed camera was set as 0.2 ms.

The condensed-phase products of a boron-based fuel-rich propellant obtained under different chamber pressures were used in this study, and collection was carried out under atmospheric pressure. The detailed information and SEM images are shown in Table 1 and Figure 2, respectively.

The formulation of the propellant was 19% hydroxyl-terminated polybutadiene (HTPB), 4% dioctyl sebacate (DOS), 4% catocene, 34% ammonium perchlorate (AP), 26% boron powder, 7.5% magnesium powder, 4% aluminum powder, and 1.5% toluene-2,4-diisocyanate (TDI).



**Figure 2.** SEM images of the condensed-phase products

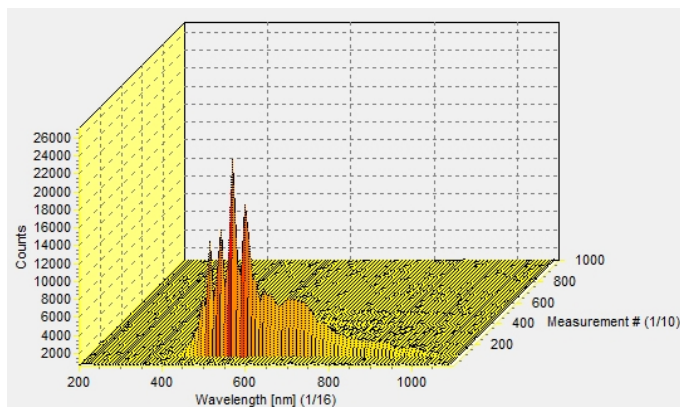
**Table 1.** Information on the condensed-phase products

Sample	Chamber pressure [MPa]	Mean particle size ( $d_{0.5}$ ) [ $\mu\text{m}$ ]	Elemental boron content [%]	Boron carbide content [%]
<i>a</i>	0.16	17.21	18.62	10.94
<i>b</i>	0.23	12.12	14.40	12.37
<i>c</i>	0.77	8.36	9.71	25.30
<i>d</i>	1.72	7.10	1.97	27.34
<i>e</i>	3.68	4.43	1.29	32.22
<i>f</i>	8.00	3.86	1.53	27.83

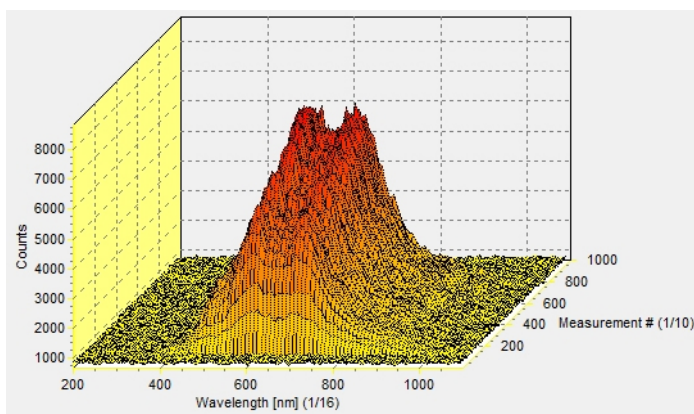
### 3 Ignition and Combustion of Boron and Boron Carbide

Boron, boron carbide, and carbon are the most important fuels in the primary condensed-phase combustion products [6]. The combustion performance of boron and boron carbide is important for the secondary combustion efficiency of ducted rockets because it is difficult for them, especially boron carbide, to release their energies completely through combustion [12, 13]. Therefore, the ignition and combustion of boron and boron carbide were studied first.

As the integration time of the spectra was very short, boron and boron carbide were ignited in air, but not initially in the combustion chamber to obtain a stronger spectrum. The three-dimensional (3D) spectra of boron and boron carbide are shown in Figures 3 and 4, respectively.

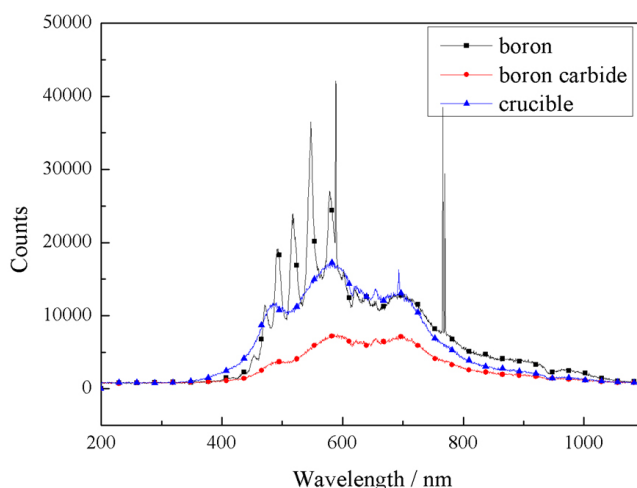


**Figure 3.** 3D spectrum of boron



**Figure 4.** 3D spectrum of boron carbide

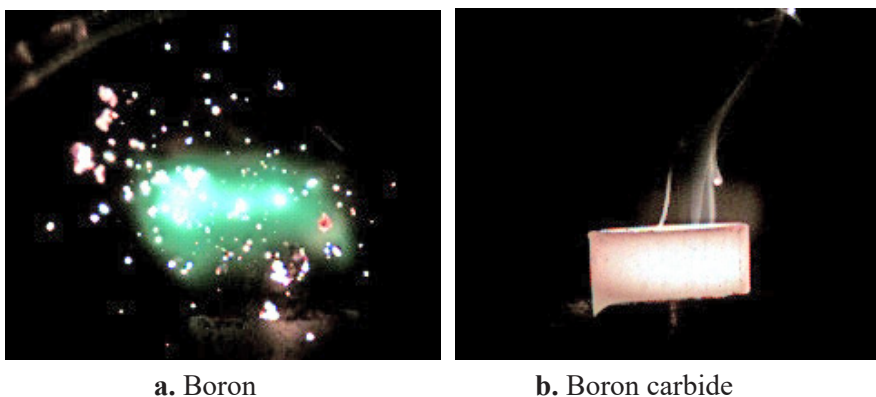
Figures 3 and 4 demonstrate a significant difference between the ignition and combustion processes of boron and boron carbide; the intensity of the spectrum shown in Figure 3 is much higher than that shown in Figure 4 whereas the duration is much shorter. In addition, the spectra at different times are almost the same, except for some differences in the signal strength for both 3D spectra. Figure 5 shows spectra of the strongest signals shown in Figures 3 and 4. To evaluate the effect of the background (mainly signals from the crucible) on the spectra, a crucible without sample was also ignited, and its spectrum with the strongest signals is also shown in Figure 5.



**Figure 5.** Spectra of pure boron, boron carbide, and the crucible

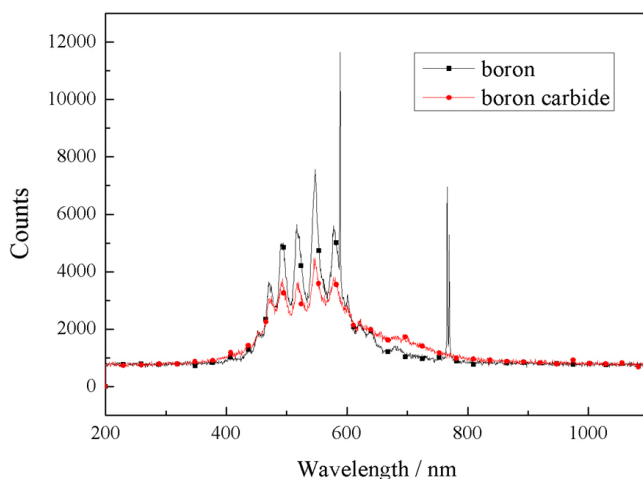
The strong peaks located at 588 nm, 766 nm, and 769 nm in Figure 5 are caused by the interference of sodium. Figure 5 shows that the combustion of boron is violent, and the peaks in the spectra resulting from the emission of  $\text{BO}_2$  agree well with those reported in the literature [14]. The spectrum from boron carbide is almost the same as that of the crucible except for the intensity, indicating that boron carbide does not burn under these conditions.

The high-speed camera photographs of the combustion of boron and boron carbide with the strongest image are shown in Figure 6.



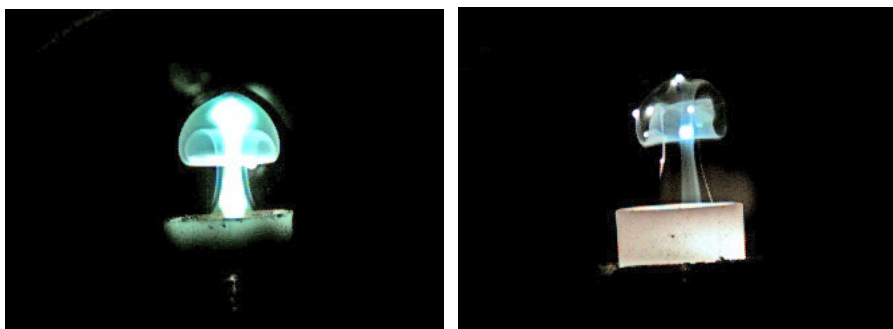
**Figure 6.** High-speed camera photographs of the combustion process in air at atmospheric pressure

Figure 6 also shows that boron underwent violent combustion and produced a bright green flame, but the combustion of boron carbide did not produce any flame. This also indicates that it is difficult to burn boron carbide [15]. Pressure plays an important role in the combustion of solid fuels, and a higher pressure would usually improve the combustion performance. Boron and boron carbide were therefore ignited in the pressurized and windowed combustion chamber under 2 MPa pressure air, and the spectra and high-speed camera photographs with the highest signals are shown in Figures 7 and 8.



**Figure 7.** Spectra of boron and boron carbide burning under 2 MPa pressure air





**Figure 8.** High-speed camera photographs of boron and boron carbide burning under 2 MPa pressure air

Figures 7 and 8 show that both boron and boron carbide underwent violent combustion in air at 2 MPa pressure, indicating that a higher pressure helps to improve their combustion. In addition, the combustion of boron is also much more violent than that of boron carbide, indicating that boron still has a better combustion performance under high pressure.

## 4 Ignition and Combustion of the Condensed-phase Products

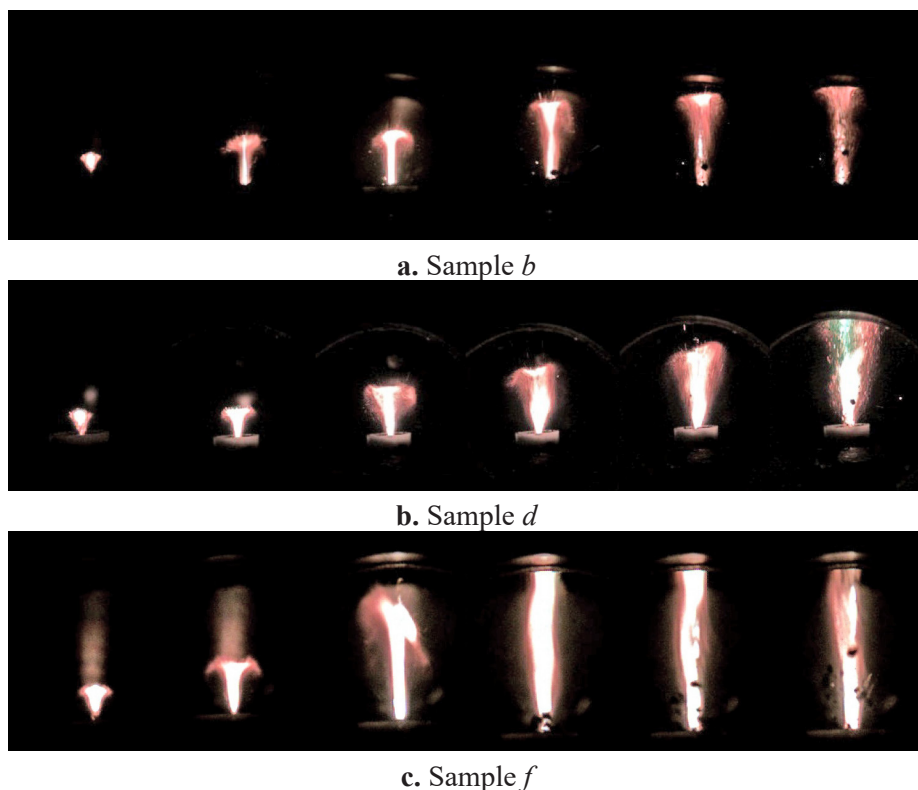
### 4.1 Ignition and combustion

The high-speed camera photographs of the combustion of samples *b*, *d*, and *f* in air at atmospheric pressure are shown in Figure 9.

Figure 8 shows that the condensed-phase products produced under a higher pressure underwent more violent combustion. No green flame was observed during the combustion of sample *b*; neither was a green flame observed at the early stage of the combustion of samples *d* and *f*. The green flame can be attributed to the combustion of boron and boron carbide, thus small amounts of boron or boron carbide take part in the combustion.

Chemical analysis of sample *b* shows the presence of a significant amount of elemental boron, but the particle size is larger because of large carbon particles, produced during the primary combustion process, in addition to agglomerated boron particles. A large particle size is unfavorable for the combustion of solid fuel; the combustion of carbon cannot provide enough energy for the combustion of boron or boron carbide, and thus would result in less vigorous combustion.

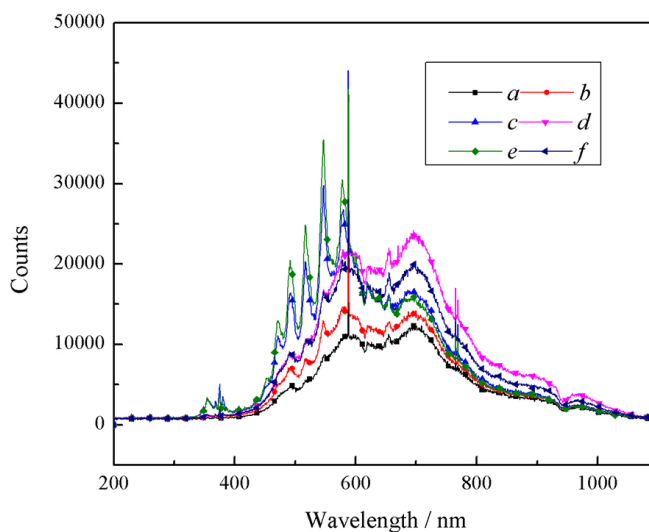




**Figure 9.** High-speed camera photographs of boron and boron carbide under 2 MPa pressure

#### 4.2 Effect of ingredients and particle size

Figure 9 shows that both the ingredients and the particle size play an important role in the combustion of the condensed-phase products, and the intensity of combustion increases with a decrease in particle size and an increase in boron carbide content. Considering that the results obtained from the high-speed camera are only qualitative, the combustion spectra obtained under atmospheric pressure (Figure 10) were used to study the combustion quantitatively. To obtain stronger spectra, the samples were ignited in atmospheric air rather than in a combustion chamber.



**Figure 10.** Combustion spectra of different products under atmospheric pressure

Figure 10 also shows that the intensity of the spectra increases with a decrease in particle size and an increase in boron carbide content, consistent with the results obtained from the high-speed camera. Figures 3-6 show that the combustion of boron is more violent than that of boron carbide; thus, the combustion of a sample containing more boron carbide should be less violent. However, the combustion performance of boron carbide in the sample may be better than that of boron.

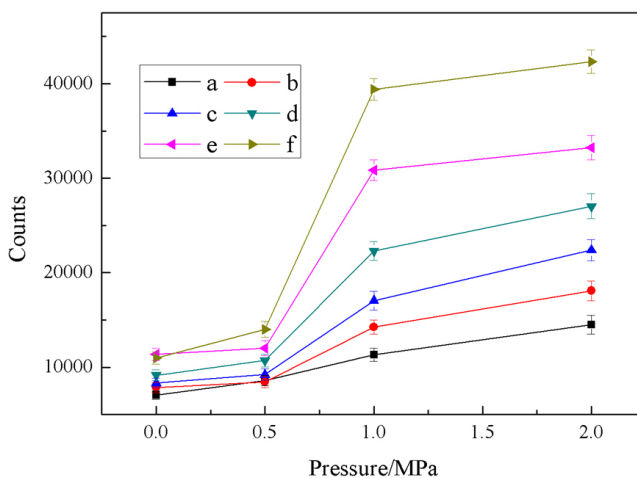
Although the heat of combustion of boron is higher than other common metallic fuels, boron suffers from ignition and combustion issues [16, 17]. Normally, boron particles are coated with a layer of boron oxide, and higher viscosity liquid boron oxide ( $\sim 1.85 \text{ Pa}\cdot\text{s}$  at 1800 K), effectively preventing the oxidizer, the ambient atmosphere, from reaching the boron fuel [18]. The layer of liquid boron oxide was found to be exceptionally stable below 1820 K because of a marked increase in the surface tension with increasing temperatures [19], resulting in a Marangoni flow towards the hot spot and a more stable liquid boron oxide layer [20]. In this study, a thicker boron oxide layer was formed on the surface of the boron particles during the primary combustion process, which is unfavorable for the re-ignition of the boron particles. Furthermore, boron particles tend to agglomerate during the primary combustion process, causing a poor combustion performance [21]. Notably, the carbide present in the combustion products mixes well with the carbon, and the combustion of

the carbon improves the combustion of the boron carbide. Therefore, samples containing more boron carbide will exhibit a better combustion performance.

In addition, although the particle size of sample *e* is larger than that of sample *f*, the intensity of the spectrum of sample *e* is higher. This is also because of the higher boron carbide content in sample *e*.

### 4.3 Effect of chamber pressure

Figures 5 and 7 show that a higher pressure has a positive effect on the combustion of boron and boron carbide. Considering that the shapes of the spectra obtained during the combustion of all of the samples are almost the same, except for their intensity, the strongest peaks, located at 547 nm, were used to characterize semiquantitatively the intensity of the combustion of the samples. Figure 11 shows the intensity of these peaks during the combustion of the samples under different pressures. To obtain comparable spectra, all of the samples were ignited in the combustion chamber.



**Figure 11.** Spectrum intensity from peak at 547 nm

Figure 11 shows that the combustion of all of the condensed-phase products is more violent under a higher pressure because of the positive correlation between the pressure and the combustion reactions of boron, boron carbide, and carbon. Both the particle size and boron carbide content under a higher primary combustion pressure were lower, resulting in a higher combustion intensity under all of the secondary pressures. Therefore, a higher primary combustion pressure is favorable for combustion efficiency.

Figure 11 also indicates that the positive effect of pressure on the combustion intensity of the primary combustion products is much more obvious under a modest pressure. The secondary combustion pressure is usually below 1 MPa; thus, a higher secondary combustion pressure is also beneficial for combustion efficiency.

## 5 Conclusions

The combustion performance of the primary condensed-phase combustion products of a boron-based fuel-rich propellant was studied. The following conclusions were made:

- (1) The combustion of the condensed-phase products originates from the combustion of carbon, but boron may not take any part in the combustion because of a thick boron oxide coating and agglomeration during the primary combustion process.
- (2) Both the particle size and the ingredients significantly affect the combustion reaction of the condensed-phase products, and a lower particle size and a higher boron carbide content would benefit the combustion reaction.
- (3) Pressure plays an important role in the combustion of the condensed-phase products, and a higher pressure in both the primary and the secondary combustion processes would improve the combustion reaction.

## Acknowledgements

This research is supported by the Key Foundation of Science and Technology on Combustion, Internal Flow and Thermal-Structure Laboratory (9140C520102150C52009).

## References

- [1] Besser, H. L.; Strecker, R. Overview of Boron Ducted Rocket Development. *Int. J. Energ. Mater. Chem. Propul.* **1991**, 2(1-6): 133-178.
- [2] Fry, R. S. A Century of Ramjet Propulsion Technology Evolution. *J. Propul. Power* **2004**, 20(1): 27-58.
- [3] Gany, A; Timnat, Y. M. Advantages and Drawbacks of Boron-fueled Propulsion. *Acta Astronaut.* **1993**, 29(3): 181-187.
- [4] Liang, D.; Liu, J.; Xiao, J.; Xi, J.; Wang, Y.; Zhang, Y.; Zhou, J. Energy Release Properties of Amorphous Boron and Boron-Based Propellant Primary Combustion Products. *Acta Astronaut.* **2015**, 112: 182-191.
- [5] Vigot, C.; Cochet, A.; Guin, C. Combustion Behavior of Boron-Based Solid Propellants

- in a Ducted Rocket. *Int. J. Energ. Mater. Chem. Propul.* **1991**, 2(1-6): 386-401.
- [6] Liu, L. L., He, G. Q., Wang, Y. H., Hu, S. Q. Chemical Analysis of Primary Combustion Products of Boron-based Fuel-rich Propellant. *RSC Advances* **2015**, 5: 101416-101426; DOI: 10.1039/C5RA13693H.
- [7] Natan, B.; Netzer, D. W. Boron Carbide Combustion in Solid-Fuel Ramjets Using Bypass Air. Part I: Experimental Investigation. *Propellants Explos. Pyrotech.* **1996**, 21(6): 289-294.
- [8] Natan, B.; Netzer, D. W. Boron Carbide Combustion in Solid-Fuel Ramjets Using Bypass Air. Part II: Theoretical Analysis. *Propellants Explos. Pyrotech.* **1997**, 22(1): 6-10.
- [9] Domnich, V.; Reynaud, S.; Haber, R. A.; Chhowalla, M. Boron Carbide: Structure, Properties, and Stability under Stress. *J. Am. Ceram. Soc.* **2011**, 94(11): 3605-3628.
- [10] Liu, L.-L.; Liu, P.-J.; He, G.-Q. Ignition and Combustion Characteristics of Compound of Magnesium and Boron. *J. Therm. Anal. Calorim.* **2015**, 121(3):1205-1212; DOI:10.1007/s10973-015-4653-6.
- [11] Ao, W.; Wang, Y.; Li, H.; Xi, J.; Liu, J.; Zhou, J. Effect of Initial Oxide Layer on Ignition and Combustion of Boron Powder. *Propellants Explos. Pyrotech.* **2014**, 39(2): 185-191.
- [12] Veith, J.; Pfitzner, M. Combustion of Boron Particles in Premixed Methane/Air Flames. *Propellants Explos. Pyrotech.* **2016**, 41(2): 260-266; DOI: 10.1002/prop.201500069.
- [13] Ao, W.; Yang, W.; Wang, Y.; Zhou, J.; Liu, J.; Cen, K. Ignition and Combustion of Boron Particles at One to Ten Standard Atmosphere. *J. Propul. Power* **2014**, 30(3): 760-764.
- [14] Spalding, M. J.; Krier, H.; Burton, R. L. Boron Suboxides Measured during Ignition and Combustion of Boron in Shocked Ar/F/O<sub>2</sub> and Ar/N<sub>2</sub>/O<sub>2</sub> Mixtures. *Combust. Flame* **2000**, 120(1): 200-210.
- [15] Poret, J. C.; Sabatini, J. J. Comparison of Barium and Amorphous Boron Pyrotechnics for Green Light Emission. *J. Energ. Mater.* **2013**, 31(1): 27-34.
- [16] Hussmann, B.; Pfitzner, M. Extended Combustion Model for Single Boron Particles – Part I: Theory. *Combust. Flame* **2010**, 157(4): 803-821.
- [17] Hussmann, B.; Pfitzner, M. Extended Combustion Model for Single Boron Particles – Part II: Validation. *Combust. Flame* **2010**, 157(4): 822-833.
- [18] Eppler, R. A. Viscosity of Molten B<sub>2</sub>O<sub>3</sub>. *J. Am. Ceram. Soc.* **1966**, 49(12): 679-680.
- [19] Shpil'rain, E. E.; Yakimovich, K. A.; Tsitsarkin, A. F. Investigation of the Surface Tension of Liquid Boron Oxide to 2000 Degrees C by the Cylinder Pulling Method. *High Temp.-High Press.* **1972**, 4(1): 67-76.
- [20] Meinköhn, D. Boron Particle Ignition and the Marangoni Effect. *Combust. Sci. Technol.* **2004**, 176(9): 1493-1536.
- [21] DeLuca, L. T.; Marchesi, E.; Spreafico, M.; Reina, A.; Maggi, F.; Rossetini, L.; Bandera, A.; Colombo, L. P. M.; Kosowski, B. M. Aggregation versus Agglomeration in Metallized Solid Rocket Propellants. *Int. J. Energ. Mater. Chem. Propul.* **2010**, 9(1): 9.