



Combustion Characteristics and Mechanism of Boron-based, Fuel-rich Propellants with Agglomerated Boron Powder

Hui-xiang XU^{1,*}, Wei-qiang PANG², Hong-wei GUO²,
Feng-qi ZHAO¹, Ying WANG¹, Zhi-hua SUN¹

¹Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Shaaxi Xi'an 710065, China

²Xi'an Modern Chemistry Research Institute, Shaaxi Xi'an 710065, China

**E-mail: xhx204@163.com*

Abstract: In order to extend the burning rate of boron-based, fuel-rich solid propellants with agglomerated boron powder, the effects of the boron content, the AP content, and of the magnesium powder content, on the burning rate and pressure exponent have been studied systematically. It has been shown that when the AP content is constant, the burning rate of the propellants increases with an increase in the agglomerated boron content. Furthermore, the burning rate and pressure exponent increase with increasing the contents of AP and magnesium powder. By means of single colour frame amplification photography and combustion wave tests, the combustion mechanism of these propellants has been investigated. It has been shown that the flame of the propellants becomes brighter by increasing the AP content, the dT/dx_{cp} and dT/dx_{gp} of the propellant FR-5 being around 6815 and 5789 °C/mm respectively, higher than those of FR-4, resulting in greater burning rates. The T_s of these propellants is above 683 °C, which is higher than the decomposition peak temperatures of agglomerated boron powder and of propellants (about 649 °C), which indicates that agglomerated boron powder is partially oxidized on the combustion surface, and the heat released from it may be beneficial to the combustion of the propellants.

Keywords: analytical chemistry, boron-based fuel-rich solid propellants, agglomerated boron powder, combustion performance, combustion mechanism

1 Introduction

In order to improve the rheological properties between amorphous boron powder and the HTPB binder, and to increase the combustion performance of boron-based, fuel-rich solid propellants, several boron powder modification methods have been investigated [1-5]. In recent years, research on the modification of boron powder processing indicates that agglomerating boron powder is a necessary step for modifying boron powder, and a detailed research method has been developed. A type of spherical particle agglomerating method had been reported [6], which involves a liquid-phase reaction process. Pang *et al.* [7] had prepared agglomerated boron powder by a water-free method, by which boron powder was wetted, stirred with a solution of a binder, and rounded to agglomerated particles in a suitable humidity. These studies suggested that the agglomerated boron powder could improve the processing properties of boron-based, fuel-rich solid propellants. In that case, one could greatly increase the solids content, including boron powder, fine AP or other materials, which would help to improve the energy and combustion performance of the propellants. Wang [8-11] had agglomerated boron powder with AP, and systematically investigated the combustion characteristics and mechanism of this propellant. In short, there are many studies on the combustion characteristics of boron-based, fuel-rich solid propellants, but there are few systematic reports dealing with the combustion characteristics and mechanism of boron-based, fuel-rich solid propellants incorporating binder agglomerated boron powder.

In this paper, the combustion characteristics of the propellants were systematically studied using spherical, agglomerated boron powder, and its combustion mechanism was analyzed. This may help to control the combustion properties.

1 Experimental

1.1 Boron surface treatment and agglomeration

Amorphous boron powder, with purity about 94-95% and median particle size about 1.88 μm , produced by PENGDA Technology Co., Ltd., Liaoning (China), was used as the raw material. A neutralized process was employed to pretreat the boron powder [12], and it was then coated with the HTPB binder in solvents. The HTPB content was about 10%.

1.2 Formulation

A 2 L vertical kneader was used to prepare the B/Mg/AP/HTPB propellant formulations which are shown in Table 1. The other materials were industrial products, amongst them catalysts belongs to the ferrocene type. The sample preparation process was the same as that of a conventional composite solid propellant. The propellant slurry was cast under vacuum, and then cured at 70 °C for 5 days.

Table 1. Formulation of propellants

No.	Composition and Content, [%]						
	HTPB System	Catocene	Mg/ 45 μm	AP/ 105 μm	AP/ 1 μm	B/ 900 μm	B/ 200 μm
FR-1	26	1	5	30	5	16.5	16.5
FR-2	24	1	5	30	5	17.5	17.5
FR-3	21.5	1	5	30	5	18.75	18.75
FR-4	25	5	5	25	5	35	0
FR-5	20	5	5	25	10	23.3	11.7
FR-6	25	5	0	30	5	23.3	11.7
FR-7	23	5	2	30	5	23.3	11.7
FR-8	20	5	5	30	5	23.3	11.7

1.3 Testing facilities and methods

The surface morphology of the boron powder was tested using a Japanese JSM-5800 scanning electron microscopy (SEM).

Thermogravimetric (TG) analysis of the samples was carried out on a TG analyzer (Model TGA2950, TA Co., USA) at a heating rate of 10 °C·min⁻¹ and an N₂ flow of 40 mL·min⁻¹.

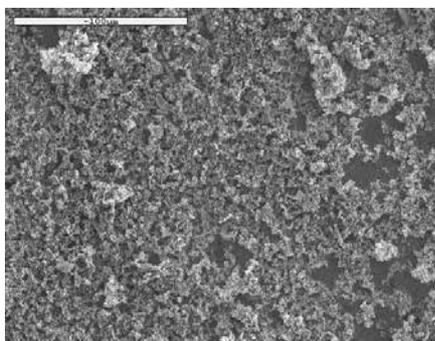
The burning rate (u_r) of the propellants was measured by the target wire method. Measurements were made using a strand in a nitrogen atmosphere with rectangular sticks of 5×5×100 mm samples coated with polyvinyl formal.

The combustion mechanisms of the propellants were investigated by means of single colour frame amplification photography, and a Π mode miniature thermocouple (width 70 μm and thickness 5 μm). The flame structures were obtained using a high-speed camera with rectangular sticks of 2×5×15 mm samples in a quad-optic transparent combustion chamber under a nitrogen atmosphere.

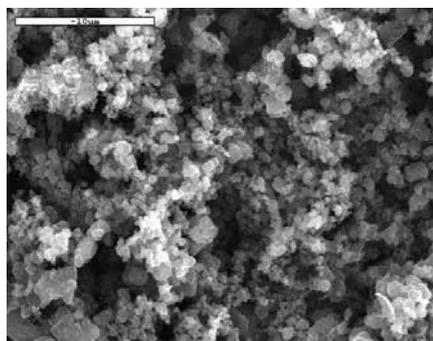
2 Results and Discussion

2.1 Effect of boron content on the burning rate of the propellants

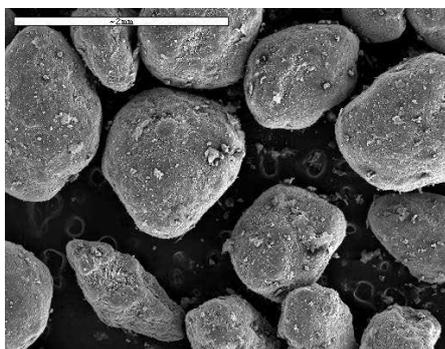
Under the same conditions, and changing the contents of HTPB and agglomerated boron powder, the effect of the boron content on the burning rate of the propellants was investigated. The agglomerated boron powder was prepared from an HTPB binder and amorphous boron powder in solvents, and two sizes of agglomerated boron powder were made, with mean particle size $900\ \mu\text{m}$ and $200\ \mu\text{m}$. The SEM photographs of the surface structure of the boron powder are shown in Figure 1 and the dependence of the burn rate on the pressure is plotted in Figure 2. The boron content from FR-1 to FR-3 was 33, 35 and 37.5% respectively, in which the HTPB content had been partially substituted, and two sizes of agglomerated boron were added in the proportion of 1:1.



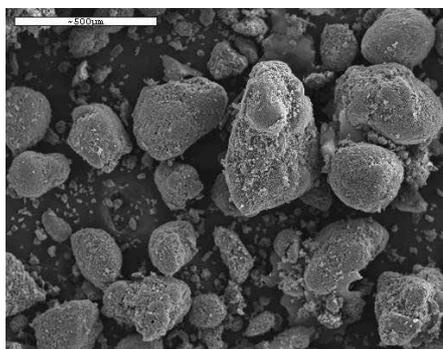
(a) $\times 500$; SEM of amorphous boron powder



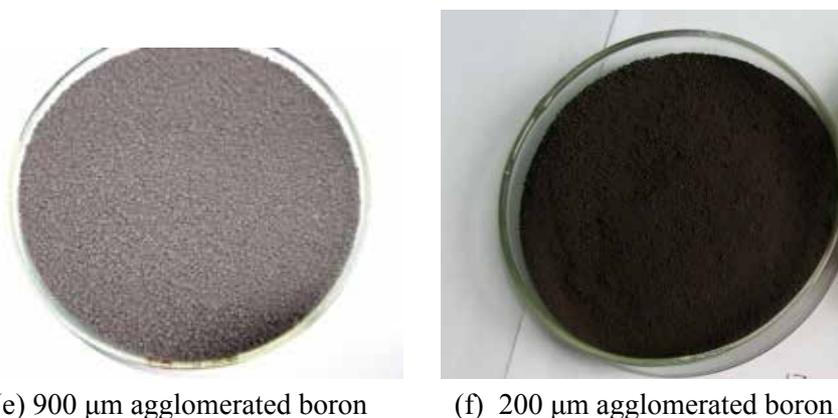
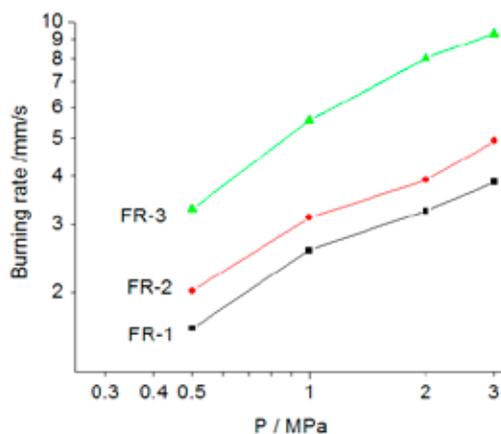
(b) $\times 4000$; SEM of amorphous boron powder



(c) $\times 30$; SEM of $900\ \mu\text{m}$ agglomerated boron



(d) $\times 80$; SEM of $200\ \mu\text{m}$ agglomerated boron

(e) 900 μm agglomerated boron(f) 200 μm agglomerated boron**Figure 1.** SEM pictures of boron powder.**Figure 2.** The dependence of burning rate on pressure for propellants with different boron powder contents. The corresponding burning rate formula are $u_{r1} = 2.361P^{0.471}$, $u_{r2} = 2.911P^{0.478}$, $u_{r3} = 5.186P^{0.583}$, respectively.

The results in Figure 1 show that the particle shape of the amorphous boron powder was irregular with size of 1-2 μm , the particle surface was not smooth, but that the particle shape of the agglomerated boron powder was regular, spherical and smooth, which is helpful for significantly increasing the amount of boron powder.

The data from Figure 2 show that, with the increase in boron powder content, the burning rate and the pressure exponent of the propellants were increased significantly.

On the one hand, the increase in boron content is accompanied by a decrease in the HTPB content. In the combustion process of a fuel-rich propellant, HTPB may decompose forming hydrocarbon compounds with short molecular chains, such as butadiene and ethylene, but the oxygen coefficient of a fuel-rich propellant is as low as 0.1-0.2, so the hydrocarbons are only partially oxidized to CO_2 during HTPB decomposition. The other gases are mostly CO and H_2O , and the rest are converted to carbon, contributing to the combustion residues. Therefore, in the primary combustion step, the decomposition of HTPB may consume a large amount of the heat released from the AP decomposition. When the HTPB content is reduced, the extra heat may increase the temperature of the condensed phase, favouring faster decomposition, and hence increasing the burning rate. At the same time, with the increase in the condensed phase temperature, the rate of gas production is increased and the concentration of the gaseous reactants will also be greatly increased, increasing the reaction rate and diffusion speed of the gas phase. This would finally affect the flame structure and enhance the premixed flame speed, resulting in a higher pressure exponent.

On the other hand, in the primary combustion zone, there would be a small amount of boron powder evolving in the exothermic reaction of the condensed phase. Therefore, with the increased boron powder content, reaction of the boron powder increases, subject to the increased burning rate of the propellants.

2.2 Effect of AP content on the burning rate of the propellants

The effect of the AP content on the burning rate of the propellants was investigated, and the results of the burning rate are shown in Figure 3, where the AP content was 30% in FR-4, and 35% in FR-5.

It has been shown that the burning rate of propellants can be greatly improved by reducing the content of the HTPB binder and increasing the AP content. Because AP is the oxidizing agent in the propellants, and the exothermic reaction between AP and the fuels maintains the combustion of the propellants. Then, with an increase in AP content, gas production and heat release both increase, so the concentration of the oxidizing gas increases, resulting in an increased reaction rate and pressure exponent in the gas phase. On the other hand, the increase in AP content will reduce the fuel content, which does not benefit the energy of the propellant.

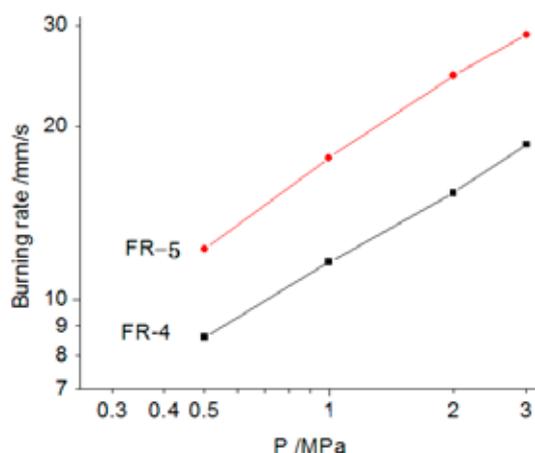


Figure 3. Effect of AP content on the combustion performance of fuel-rich solid propellants. The burning rate formula are $u_{r4} = 11.56 P^{0.43}$, $u_{r5} = 17.31 P^{0.48}$, respectively.

2.3 Effect of Mg content on the burning rate of the propellants

The effect of Mg content on the burning rate of the propellants was investigated, and the results of the burning rate are shown in Figure 4, where the Mg content was 0, 2 and 5% in FR-6, FR-7, and FR-8, respectively.

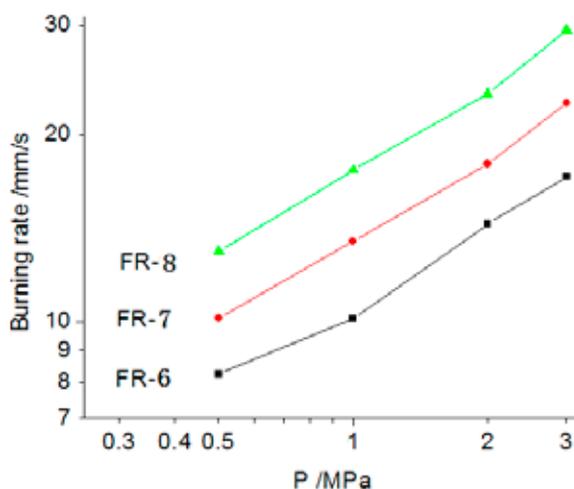


Figure 4. Effect of Mg content on the combustion performance of fuel-rich solid propellants. The burning rate formula are $u_{r6} = 10.67P^{0.41}$, $u_{r7} = 13.58P^{0.43}$, $u_{r8} = 17.56P^{0.45}$, respectively.

It has been shown that the burning rate and pressure exponent of propellants can be improved by adding Mg powder, and reducing the content of the HTPB binder. This might be due to:

- (1) The reactivity of Mg being higher than other fuels, and the ignition temperature of the fuel-rich propellant with Mg would be reduced.
- (2) The boiling point of Mg is low, so Mg powder is easily vaporized. When Mg powder is added to propellants, combustion of the Mg starts by vaporization of the condensed phase. So its combustion flame is close to the combustion surface, and the heat feedback from the flame to the condensed phase is increased.
- (3) The burning rate of Mg is faster than that of the other components, which is helpful for converting the chemical energy of Mg into heat, increasing the temperature of the condensed phase and of the gas phase surrounding the Mg powder, and accelerating the thermal decomposition and combustion of the propellants.

Consequently, Mg powder can increase the burning rate.

2.4 The combustion mechanism of boron-based, fuel-rich solid propellants with agglomerated boron powder

Flame photographs of the propellants at 1 MPa were obtained using a high-speed camera, and are shown in Figure 5.

Since a lot of smoke was produced in the combustion process of boron-based, fuel-rich solid propellants, which affected the clarity of the pictures, it was difficult to see a clear flame, and some photographs show only hot metal particles, as in picture (a).

Compared with picture (a) (FR-4), the burning surface of FR-5 (b) is a continuous, long flame. There are black particles surrounded by flames in the flame zone, which are due to decomposing of boron powder particles, whilst the AP flame is spouting from gaps in the boron powder particles. With increasing AP content and a reduction in the HTPB system, the AP content increases significantly in the AP and HTPB aggregating area, the heat of the AP decomposition and the oxidation gas concentration also increase, and the fast burning is helpful in the mixing and combustion of the different decomposition products. Therefore, increasing AP content contributes to the combustion of fuel-rich propellants.

In picture (c), the flame is bright, being the highest in the tested samples. Due to the presence of boron powder agglomeration, the brighter flame is discontinuous in the combustion zone, but the flame is longer and spouting violently for the presence of metal particles. Therefore, adding flammable

metal Mg powder, and reducing the inert HTPB binder system, can significantly promote the combustion properties of the boron-based, fuel-rich propellant.



(a) FR-4

(b) FR-5



(c) FR-8

Figure 5. Flame photographs of fuel-rich solid propellants.

The temperature distribution of the combustion wave was also tested at 1 MPa, and the T-x curves of the propellants are shown in Figure 6.

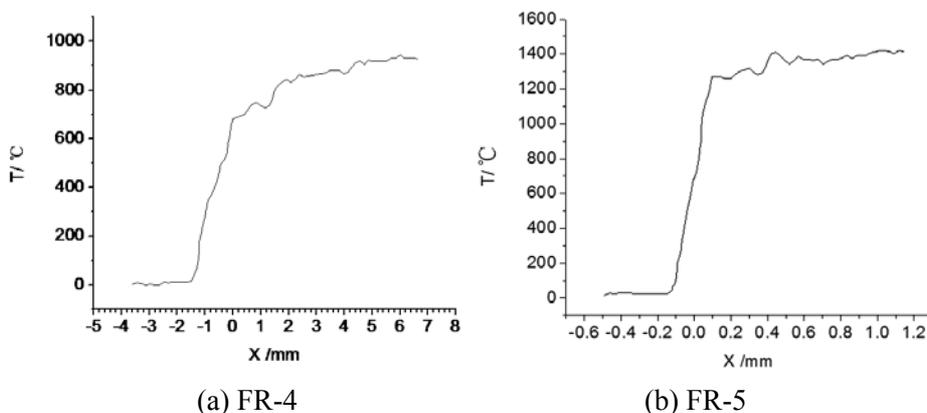


Figure 6. Combustion wave T-x curves of the propellants.

The surface temperature (T_s), flame temperature (T_f) and temperature distance gradient (dT/dx) of the propellants are shown in Table 2, where dT/dx is the gradient of the temperature change per unit distance.

Table 2. Combustion wave data for propellants

No.	T_s [°C]	T_f [°C]	dT/dx_{cp} [°C/mm]	dT/dx_{gp} [°C/mm]
FR-4	689	821	4868	485
FR-5	683	1267	6815	5789

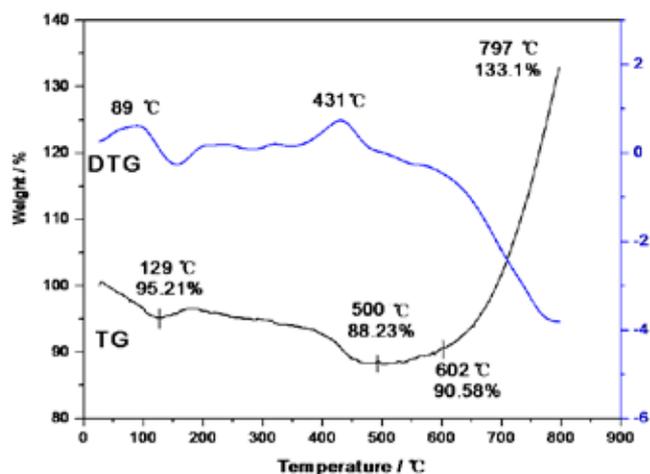
Note: dT/dx_{cp} is dT/dx of the condensed phase, dT/dx_{gp} is dT/dx of the gas phase.

The TG-DTG curves of agglomerated boron powder and FR-4 are shown in Figure 7.

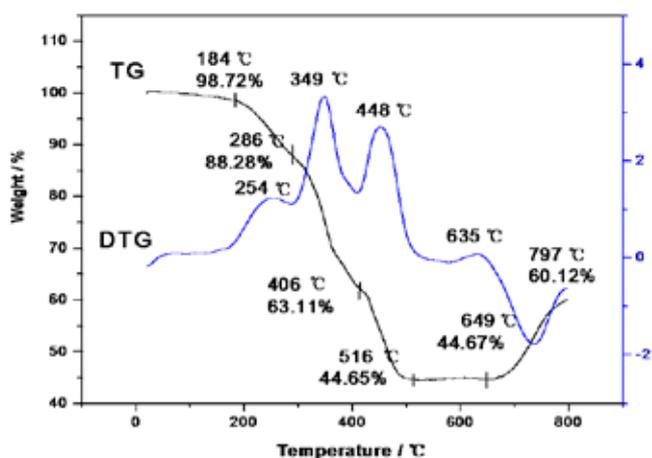
The results of these curves and these data show that:

- (1) Comparing FR-5 with FR-4, the T_f , dT/dx_{cp} and dT/dx_{gp} of FR-5 are higher than those of FR-4, and the intensity of the flame is greater than that of FR-4. This indicates that the AP content has an important effect on the gas phase combustion, enhancing the heat feedback of the gas phase, and increasing the burning rates of the propellants.
- (2) For agglomerated boron powder with HTPB, the TG-DTG peak from 350 °C to 500.15 °C results from the decomposition of the HTPB network structure, since depolymerization, cyclization and crosslinking reactions of the HTPB binder takes place from 250 °C to 410 °C. For the TG-DTG curve of FR-4, the

main decomposition peak at 350 °C is due to the exothermic decomposition of AP, whilst the peak at 448.5 °C is due to the thermolysis of HTPB, and the weight increase from 649 °C is due to the oxidation of boron. Consequently, the T_s of these propellants is higher than the main decomposition temperatures of the agglomerated boron powder and the propellants, which indicates that decomposition reactions occur at the surface. HTPB, AP and boron participate in the oxidation reaction, and the oxidation of boron may be beneficial to the combustion of propellants by greater heat release.



(a) Agglomerated boron



(b) FR-4

Figure 7. TG-DTG curves.

3 Conclusions

- (1) When the AP content is constant, increasing the boron powder content increases the burning rate of boron-based, fuel-rich propellants.
- (2) Increasing the contents of AP and Mg powder can increase the burning rate and the pressure exponent of propellants.
- (3) By increasing the AP content, the flame of the propellants is brighter. dT/dx_{cp} and dT/dx_{gp} of the propellant FR-5 is around 6815 and 5789 °C/mm respectively, higher than those of FR-4, and resulting in an increase in burning rate.
- (4) In order to improve the propellant flame structure, and promote the condensed phase and gas phase reactions significantly, the AP content should be selected appropriately.
- (5) The T_s of propellants is above 683 °C, and is higher than the main decomposition temperatures of agglomerated boron powder and propellants, about 448.5 °C, which indicates that agglomerated boron powder can participate in the oxidation reactions, being beneficial to the combustion of propellants with greater heat release.

Acknowledgements

We are grateful to Dr. Yan Qi-long and Dr. Anthony Bellamy, the Linguistic Editor of CEJEM, for the careful modification of grammar and spelling in the paper.

4 References

- [1] Nieder E.G., *Chemical Passivation of Amorphous Boron Powder*, US Patent 4 637 847, **1987**.
- [2] Li S.F., Jin R.C., Surface Coating of Boron Powder and Its Effect (in Chinese), *Chin. J. Energ. Mater. (Hanneng Cailiao)*, **1996**, 4(3), 102-108.
- [3] Pang A.M., Zheng J., Xiao J.W., Investigation into the Feasibility of Boron Powder Burning in the Second Combustor of Ducted Rocket Motor (in Chinese), *Chin. J. Energ. Mater. (Hanneng Cailiao)*, **2004**, 12 (Suppl.), 185-188.
- [4] John C., *Coating of Boron Particles*, US Patent 4 915 753, **1988**.
- [5] Xu H.X., Zhao F.Q., Li Y.H., Effect of Neutralised Boron Powder on the Rheological Property of B/HTPB (in Chinese), *Chin. J. Energ. Mater. (Hanneng Cailiao)*, **2007**, 15(4), 341-344.
- [6] Macri B.J., *Process for Making Spheroidal Agglomerates*, US Patent 3 646 174 A, **1972**.
- [7] Pang W.Q., Zhang J.Q., Hu S.Q., Dang J.B., Guo J.Y., The Influence of

- Agglomerated Boron on Burning Rate of Fuel-Rich Solid Propellant (in Chinese), *Chin. J. Explos. Propellants (Huozhayao Xuebao)*, **2006**, 29(3), 20-22.
- [8] Wang Y.H., Li B.X., Hu S.Q., Xiao X.Y., Effect of AP Particle Size and Coating on Combustion of Boron (in Chinese), *J. Solid Rocket Technol. (Guti Huojian Jishu)*, **2004**, 27(1), 50-52.
- [9] Wang Y.H., Li B.X., Zhang X.H., Wu W.E., Study on Burning Surface Sedimentary Deposit of Boron-based Fuel-rich Propellant (in Chinese), *J. Solid Rocket Technol. (Guti Huojian Jishu)*, **2006**, 29(2), 120-123
- [10] Wang Y.H., Li B.X., Hu S.Q., Li J.X., Study on Combustion Mechanism of Fuel-rich Propellant Holding Boron Coated with AP (in Chinese), *Chin. J. Explos. Propellants (Huozhayao Xuebao)*, **2004**, 27(2), 44-47.
- [11] Hu S.Q., Li B.X., Wang Y.H., Wei Q., Combustion Characteristics of Boron-based Fuel-rich Propellant at Low Pressure (in Chinese), *J. Propul. Technol. (Tuijin Jishu)*, **2002**, 23(6), 518-520.
- [12] Xu H.X., Zhao F.Q., Li X.Y., Purification of Amorphous Boron Powder with Solvents (in Chinese), *Chin. J. Explos. Propellants (Huozhayao Xuebao)*, **2007**, 30(2), 8-12.

