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Research Article

Application of $Al/B/Fe_2O_3$ Nano Thermite in Composite Solid Propellant

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Abstract

Hydroxyl-terminated polybutadiene (HTPB) propellant were prepared with different content of $Al/B/Fe_2O_3$ nano thermite, and the mechanical, thermal and energetic performances were studied. $Al/B/Fe_2O_3$ nano thermite exhibited good compatibility with HTPB and dioctyl sebacate (DOS) through differential scanning calorimetry (DSC) tests. Mechanical experiments show that the mechanical properties of HTPB propellant could be improved by the addition of a small quantity of $Al/B/Fe_2O_3$ nano thermite, compared with the absence of $Al/B/Fe_2O_3$ nano thermite. For example, with the addition of 3% $Al/B/Fe_2O_3$ nano thermite, the tensile strength and elongation of propellant had the increase of 15.3% and 32.1%, respectively. Thermal analysis indicated that the decomposition of ammonium perchlorate (AP) in HTPB propellant could be catalyzed by $Al/B/Fe_2O_3$ nano thermite, the high-temperature exothermic peak of AP was shifted to lower temperature by 70.8 °C when the content of $Al/B/Fe_2O_3$ nano thermite was 5%, and the heat released was enhanced by 70%. At the same time, the heat of explosion of HTPB propellant could also be enhanced by the addition of $Al/B/Fe_2O_3$ nano thermite. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: $Al/B/Fe_2O_3$ nano thermite; HTPB propellant; mechanical performance; thermal analysis; heat of explosion

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1. Introduction

Nano thermites are a class of energetic materials that are composed of nano-sized metal fuel and oxidizer particles. During the past years, the most widely reported thermites are: Al/Fe_2O_3, Al/CuO, $Al/KMnO_4$, Al/WO_3, Al/MoO_3, etc. [1-5]. As the nanoscale in particle size reduces the mass transport distance between the fuel and oxidizer, and the high ratio of surface area to volume of the nanoparticles leads to more intimate fuel/oxidant contact, the rate of energy release of nano thermites is primarily controlled by chemical kinetics rather than mass transport. Therefore, the energy release of these materials is improved greatly, and the reaction rate becomes faster than that of the conventional energetic materials, simultaneously. For example, the energy density of Al/Fe_2O_3 is 16.5 kJ/cm^3, which is two times higher than that of trinitrotoluene (TNT) with 7.5 kJ/cm^3 [6].

In composite solid propellant, reactive metal powders such as Al, B and Mg are often used to enhance the specific impulse, density and to improve the combustion property [7]. As the su-

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perior energetic performance, nano thermites can be added in propellant to replace some of the metal powder to improve the performance of solid propellant. Moreover, ammonium perchlorate (AP) is a widely used oxidizing agent in solid rocket propellant, and the thermal decomposition process of AP can be catalyzed by nanocrystalline transition metal oxides such Fe_2O_3, which is also a common used oxidizer in nano thermites [8]. Hence, the addition of Fe_2O_3 based nano thermites can improve the combustion performance of propellant at the same time.

In our previous work, the Al/B/Fe_2O_3 nano thermites were prepared by a sol-gel synthetic approach combined with an ultrasonic method [9]. The test results showed that the samples were uniformly compounded and indeed energetic, furthermore, the materials were also relatively insensitive to standard impact. Therefore, it can be expected to replace a part of Al by Al/B/Fe_2O_3 nano thermites to improve the performance of Hydroxyl-terminated polybutadiene (HTPB) propellant. To be applied in propellant, the chemical compatibility between Al/B/Fe_2O_3 nano thermite and binder system was first studied to ensure safety, and then the mechanical, thermal and energetic performances of propellant with different content of Al/B/Fe_2O_3 nano thermite were also studied.

2. Materials and Methods

2.1. Materials

HTPB (OH value 0.72 mmol/g) with a molecular weight of 2800, AP with an average diameter of 250 μm and 100 μm were supplied by Liming Research Institute of Chemical Industry, Henan, China dioctyl sebacate (DOS) and isophorone diisocyanate (IPDI, NCO index: 8.99 mmol/g) were obtained from Bayer. Al/B/Fe_2O_3 nano thermites were prepared by ourselves [9]. The Al fuel has an 80 nm average diameter and the B fuel has a 15 μm average diameter. Both were supplied by Nano Material Engineering Company (Jiaozuo, China).

2.2. Preparation of Al/B/Fe_2O_3 nano thermite

A detailed propellant composition is provided in Table 1. For preparation of propellants, first Al/B/Fe_2O_3 nano thermite were dispersed in a mixture consisting of HTPB and dioctyl sebacate (DOS) for 20 min at 60 °C for wetting. Then Al, AP and curing agent isophorone diisocyanate (IPDI) were subsequently added and mixed thoroughly, followed by degassing in a vacuum oven at 30 °C. The propellant slurry was finally being poured into a mold, and cured in 60 °C for 7 days.

2.3. Characterization methods

Chemical compatibility was studied by differential scanning calorimetry (DSC), the difference values of the decomposition peak temperature (ΔT_p) between mixed materials were used to determine the chemical compatibility of two materials [10]. The mass ratio of Al/B/Fe_2O_3 nano thermite and HTPB or DOS was 1:1. Table 2 shows the evaluated standard

Table 1. Composition and serial numbers of propellants

Serial number	Composition（wt. %）					
	HTPB	IPDI	DOS	Al	AP	Al/B/Fe_2O_3
1	9.26	0.74	5	18	67	0
2	9.26	0.74	5	17	67	1
3	9.26	0.74	5	15	67	3
4	9.26	0.74	5	13	67	5

Table 2. Evaluated standard of compatibility for explosive and contacted materials

Criterial ΔT_p/°C	Rating	Note
≤2	A	compatible or good compatibility
3~5	B	slightly sensitized or fair compatibility
6~15	C	sensitized or poor compatibility
≥15	D	hazardous or bad compatibility

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of compatibility for explosive and contacted materials.

The mechanical test of dumb-bell specimens were measured with a tensile testing machine (Instron-6022, Shimadzu Co., Ltd.) at a crosshead speed of 100 mm/min at room temperature. Five specimens were tested for each sample to obtain average values. Thermal performance was tested by and differential scanning calorimetry (DSC) (METTLERTOLED, United States), from room temperature to 1000 °C at a heating rate of 10 °C/min under N_2 atmosphere. The heats of explosive of the propellant samples were evaluated in a N_2 atmosphere using the Parr 6200 Calorimeter (Parr Instrument Company, United States).

3. Results and Discussion

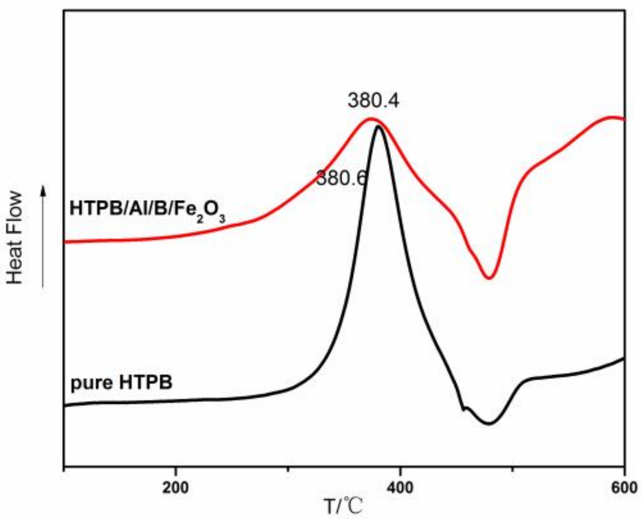
3.1. Compatibility between Al/B/Fe_2O_3 nano thermite and HTPB and DOS

DSC method is a widely used method to estimate the compatibility between energetic materials [11]. The DSC curves of HTPB, DOS and their mixtures with Al/B/Fe_2O_3 nano thermite were shown in Figure 1. From the decomposition peak observed on the curves, ΔT_p can be calculated, $\Delta T_p = T_{p1} - T_{p2}$, where T_{p1} is the maximum exothermic peak temperature of single system; T_{p2} is the maximum exothermic peak temperature of mixture system.

The results were shown in Figure 3. It can be seen in Figure 3 that the ΔT_p between HTPB and corresponding mixture is 0.2 °C while it is 1.5 °C between DOS and corresponding mixture. According to tab.2, the results indicate that the compatibility ratings are both A for the two mixtures [11], Al/B/Fe_2O_3 nano thermite has good compatibility with both HTPB and DOS, and it can be used in HTPB propellant.

3.2. Effects of Al/B/Fe_2O_3 nano thermite on the mechanical properties of HTPB propellant

Figure 2 shows the mechanical properties of propellant prepared with different contents of Al/B/Fe_2O_3 nano thermite. With the increasing content of Al/B/Fe_2O_3 nano thermite, both tensile strength and elongation of propellant raise at first and reduce later. Compared with the propellant with no Al/B/Fe_2O_3 nano thermite (sample 1), the tensile strength and elongation of propellant prepared with 3% Al/B/Fe_2O_3 nano thermite (sample 3) have the increase of 15.3% and 32.1% respectively. As is prepared by sol-gel method, few hydroxyl groups will exist on the surface of Al/B/Fe_2O_3 nano thermite though it has been heat-treated to 350 °C before use [12]. The hydroxyl groups react with the curing agent IPDI during the curing process, and the extra crosslink points will be formed on the surface of Al/B/Fe_2O_3 nano thermite, accordingly the mechanical properties are enhanced. As the content of Al/B/Fe_2O_3 nano thermite continue to increase, more surface hydroxyl groups participate in the curing reaction, which leads to an incomplete network in propellant, and the mechanical properties reduce correspondingly.



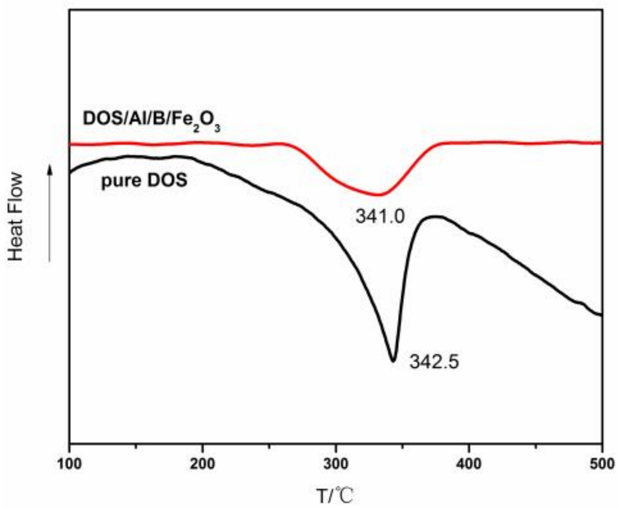


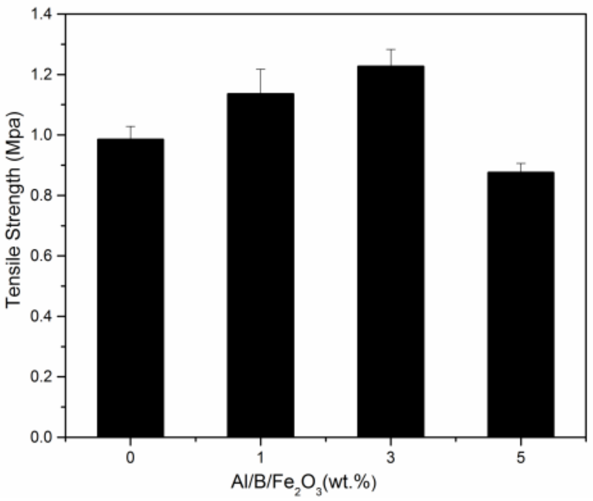
Figure 1. DSC curves of HTPB, DOS and their mixtures with Al/B/Fe_2O_3 nano thermite

3.3. Effects of Al/B/Fe_2O_3 nano thermite on the thermal properties of HTPB propellant

The DSC curves of HTPB propellant samples prepared with different contents of Al/B/Fe_2O_3 nano thermite are presented in Figure 3. Three exothermic peaks can be seen on the DSC curve of sample 1 at the temperature of 319.1, 375.3 and 423.4 °C, and correspond to the decomposition of HTPB, low-temperature decomposition of AP and high-temperature decomposition of AP, respectively.

As the nano structure and the existence of Fe_2O_3, Al/B/Fe_2O_3 has a positive effect on the decomposition of AP primarily [13]. The DSC curves of sample 2, 3 and 4 show a noticeable difference in the decomposition patterns of AP. In the DSC curves, the high-temperature exothermic peaks of AP in sample 2, 3 and 4 are shifted to lower temperature compares with sample 1, which indicates Al/B/Fe_2O_3 nano thermite exhibits catalytic activity on the thermal decomposition of AP effectively, and has little effect on the decomposition of HTPB. Meanwhile, as the increasing content of Al/B/Fe_2O_3, the exothermic peaks of AP become sharp and higher, which indicates a faster decomposition rate and higher heat release [14].

Table 4 shows the thermal parameters of four samples. Compares with the propellant pre-



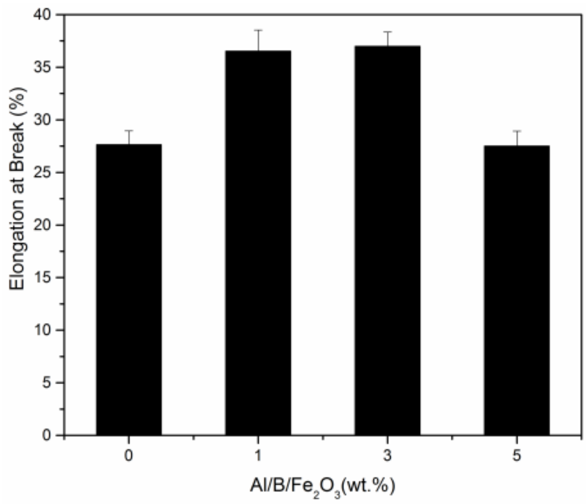


Figure 2. Mechanical properties of propellant prepared with different contents of Al/B/Fe_2O_3 nano thermite

Table 3. ΔT_p calculated from the DSC curves and the evaluation results

System		Peak temperature			Rating
Mixture System (1:1)	Single system	T_{p1} /°C	T_{p2} /°C	ΔT_p /°C	-
Al/B/Fe_2O_3-HTPB	HTPB	380.4	380.6	0.2	A
Al/B/Fe_2O_3-DOS	DOS	341.0	342.5	1.5	A

Table 4. Thermal parameters of four samples

Serial number	Content of Al//B/Fe_2O_3 /%	High-temperature exothermic peaks of AP / °C	Heat release (ΔH) (J/g)
1	0	423.4	958.4
2	1	372.1	1502.7
3	3	364.3	1598.0
4	5	352.6	1629.3

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pared with no Al/B/Fe_2O_3 nano thermite, the high-temperature exothermic peak of AP is shifted to lower temperature by 70.8 °C when the content of Al/B/Fe_2O_3 nano thermite is 5%, and the heat released is enhanced by 70%. However, the exothermic peak of thermite reaction can be hardly observed as the content of Al/B/Fe_2O_3 nano thermite is much lower than that of AP.

3.4. Effects of Al/B/Fe_2O_3 nano thermite on the heat of explosion of HTPB propellant

From Table 5, it can be seen that the heat of explosion of propellants prepared with Al/B/Fe_2O_3 nano thermite are higher than that with no Al/B/Fe_2O_3 nano thermite. Two reasons can be responsible for this result, on the one hand, the addition of Al/B/Fe_2O_3 nano thermite catalyzes the decomposition of AP in propellant, which increased the heat release of AP; on the other hand, the heat release of thermite reaction also makes the heat of explosion higher.

4. Conclusions

Al/B/Fe_2O_3 nano thermite has good compatibility with HTPB and DOS, and it can be used in HTPB propellant. Both tensile strength and elongation of the propellant samples show a tendency of raise at first and reduce later as the increasing Al/B/Fe_2O_3 nano thermite content. The tensile strength and elongation of propellant prepared with 3% Al/B/Fe_2O_3 nano thermite have the increase of 15.3% and 32.1% respectively compared with the propellant with no Al/B/Fe_2O_3 nano thermite. The decomposition of AP in HTPB propellant can be catalyzed by Al/B/Fe_2O_3 nano thermite. The high-temperature exothermic peak of AP is shifted to lower temperature and the heat released is enhanced with the addition of Al/B/Fe_2O_3 nano thermite. The heat of explosion of HTPB propellant can also be enhanced by the addition of Al/B/Fe_2O_3 nano thermite.

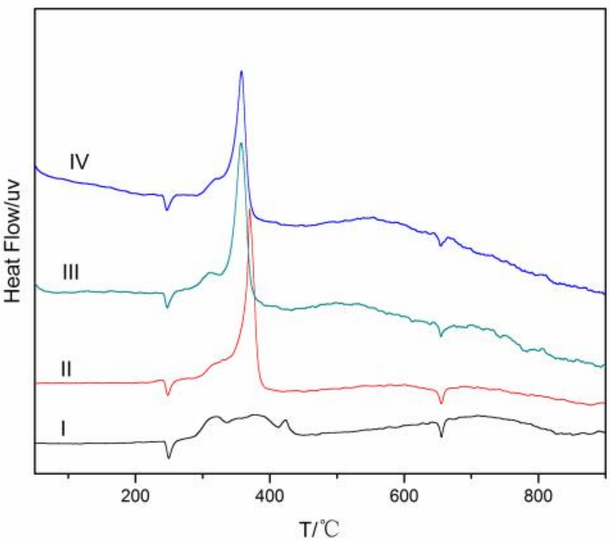

Figure 3. DSC curves of propellants prepared with different content of Al/B/Fe_2O_3 nano thermite

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Table 5. Heat of explosion of propellant samples

serial number	heat of explosion /$MJ \cdot kg^{-1}$
1	6.10
2	6.62
3	6.91
4	7.45

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