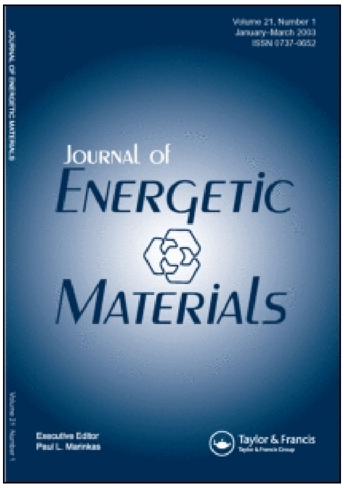

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Generation of BN in the Combustion Residue of Boron-Containing Propellant

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Residue analysis of boron-containing propellant burned in the primary and aft-mixing combustors of a solid propellant ramjet (SPRJ) indicated that a considerable amount of boron nitride (BN) was created in addition to the main product of B_2O_3. The formation heat of BN is far less than that of B_2O_3, which brings some disadvantage to the heat release of boron. Ignition and combustion of boron are carried out in an oxygen bomb Calorimeter. Thermoanalysis, X-ray diffraction, elementary analysis, and X-ray photoelectron spectroscopy are adopted to investigate the source of BN, the effect of air pressure, and the effect of oxidizers. The results show that the output of BN increases with the rising of air pressure, N_2 is proved to be the main origin of elemental nitrogen in forming BN, and a competition effect exists between the oxidation and nitrification of boron.

Keywords: Boron-containing solid propellant, boron nitride, residue analysis

Introduction

Burning of a boron-containing propellant in a solid propellant ramjet (SPRJ) may leave some residue in the primary and aft-mixing combustors [1, 2]. To study the burning property of boron, sampling of residue was made in different parts of the chambers. X-ray diffraction

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(XRD) indicates that the components of the residue include B_2O_3, BN, and B_4C, besides some unburned boron. The most remarkable observation is that a considerable amount of BN was found in all XRD charts. Hereby, we believe that, during the burning of boron-containing propellant, some portions of boron are oxidized to boron oxide by releasing a lot of energy, while some others are taken into reaction by forming BN, which is also comparative and as important. However, the latter has not received much attention and is seldom studied. Since significant differences exist between the oxidation and nitrification reactions of boron from an energetic view, it is necessary to do more investigation on the generation mechanism and physicochemical properties of boron nitride. Experiments are carried out in an oxygen bomb Calorimeter to get the combustion residue of boron. The content of BN as well as B_2O_3 was examined by instrumental analysis methods such as XRD, X-ray photoelectron spectroscope (XPS), and elementary analysis (EA). Based on the experimental results, some questions such as the source of BN, the effect of air pressure, and the effect of coating materials on the output of BN are discussed.

Physicochemical Properties of BN

Boron nitride is a white, heat-enduring substance [3]. It is structurally analogous and isoelectronic with C_2 which has 12 outside electrons. So the physicochemical properties of boron nitride are very similar to those of carbon. There are two structures of crystal BN: hexagonal (like graphite) and a face-centered cube (like diamond). The form of BN found in combustion residue is mainly a hexagonal crystal, with each lattice including four atoms. It has layered structures like graphite. In every layer B and N atoms are combined by an sp_2 orbit with a bond length of 144.6 pm (much shorter than ordinary B-N bond length of 154 pm). Between two layers, every B atom is opposite to one N atom by 333.0 pm of layer distance. It is believed by some people that, in BN, boron and nitride are partially double bonded. A ^{11}B NMR experiment further confirms this. Hexagonal crystal BN has a density of $2.25 \times 10^3\,\mathrm{kg/m^3}$, high melting point, and good qualities as a solid lubricant.

From a thermodynamic point of view, the formation reactions of both BN and B_2O_3 are exothermic. The value of the standard formation enthalpy of BN can be estimated by devising the following reaction steps [4]:

$$\begin{tikzcd} B(s) + 1/2N_2(g) \arrow[r, "A"] \arrow[rrr, bend right, "\Delta_f Hm"'] & B(g) + N(g) \arrow[r, "D"] & BN(g) \arrow[r, "S"] & BN(s) \end{tikzcd}$$

where A is atomic energy. $A_{(B)} = 554.8$ kJ/mol, $A_{(N)} = 472.8$ kJ/mol, D is bond energy, $D_{(B\text{-}N)} = -395.4$ kJ/mol, and S is crystal energy, and $S_{(BN)} = -882.2$ kJ/mol. Then the standard formation enthalpy of BN can be calculated:

$$\Delta_f H_m(\mathrm{BN}) = A_{(B)} + A_{(N)} + D_{(B-N)} + S_{(BN)} = -250\,\mathrm{kJ/mol}.$$

In the same way we can get the standard formation enthalpy of B_2O_3:

$$\begin{tikzcd} 2B(s) + 3/2O_2(g) \arrow[r, "A"] \arrow[rrr, bend right, "\Delta_f Hm"'] & 2B(g) + 3O(g) \arrow[r, "D"] & B_2O_3(g) \arrow[r, "S"] & B_2O_3(s) \end{tikzcd}$$

where $A_{(B)} = 554.8$ kJ/mol, $A_{(O)} = 249.4$ kJ/mol, $D_{(B2O3)} = -2736.3$ kJ/mol, $S_{(B2O3)} = -397.5$ kJ/mol, $\Delta_f H_m$ $(B_2O_3) = 2 \times A_{(B)} + 3 \times A_{(O)} + D_{(B2O3)} + S_{(B2O3)} = -1276$ kJ/mol.

It is obvious that the formation heat of BN is far less than that of B_2O_3. So much of the BN product in the residue of boron combustion is not what we expect.

Experiment

Thermoanalysis

A thermogravimetry experiment was carried out on pure boron under an atmosphere of high-purity nitrogen. The temperature rose from the lab temperature to 1000 °C by 10/min. TG and DTG curves were obtained as shown in Figure 1.

Coating and Combustion of Boron

To get better ignition and combustion of boron, we first treated it by surface treating. Two kinds of materials, AP(NH_4ClO_4) and KP($KClO_4$), were used in the experiment. They are both strong oxidizers. The twice-crystallization method was adopted to prepare the coated boron [5], which we labeled B^{AP} and B^{KP}.

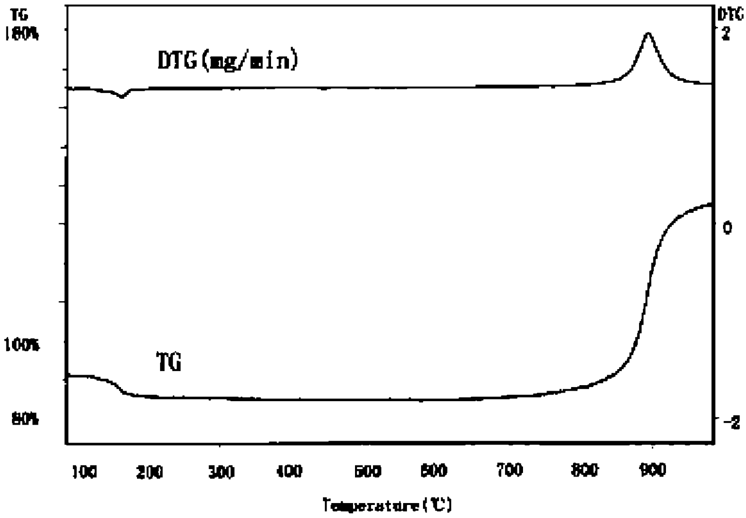

Figure 1. Thermogravimetry curve of boron under high-purity nitrogen.

Ignition and combustions were processed in an oxygen bomb Calorimeter. About 0.5 g of a sample was pressed to slice form and burned every time. The bomb was inflated with oxygen or air under some pressure. The experiments were divided into three groups:

A. B^{AP} was combusted under 0.39 MPa oxygen to study if nitrogen of the component contribute to the formation of BN.
B. B^{AP} was combusted under four different air pressures of 0.59, 0.98, 1.47, 2.25 (MPa), to study the effect of air pressure on the formation of BN as well as B_2O_3.
C. B^{AP} and B^{KP} were combusted separately under the same air pressure of 0.59 MPa to study the effect of oxidizers.

The residue was analyzed with the following instruments [6]:

1. XRD: D/Max-rA rotation anode X-ray diffraction instrument (made in Japan).
2. EA: Elementar Varit EIII elementary analysis (made in Germany).
3. XPS: ESCALAB MK-II X-ray photoelectron spectroscope (English VG company).

Discussion

Source of BN

When a boron-containing propellant is combusted in the SPRJ, a lot of aft-mixing air is in-breathed, which makes it easy for boron to contact directly with nitrogen. Chemical combination of boron and nitrogen is considered to be the most probable means of BN formation. Meanwhile, some components of the boron-containing propellant such as AP have some elemental nitrogen. Whether or not it has an effect on the formation of BN also requires discussion.

A thermogravimetry experiment on boron in the presence of high-purity nitrogen gives strong evidence that boron can react directly with nitrogen when heated. It can be seen from Figure 1 that the TG curve begins to rise at 800°C and rises sharply at 900 °C−950 °C. When the temperature reaches 1000°C, the trend of up−rise slows down. During the entire period, increase of the mass adds up to more than 40%. Since only boron and nitrogen, two substances, exist, we can infer that the increase of the mass is a result of the creation of unvolatilizable BN.

In experiment A, B^{AP} was used since 12% elemental nitrogen is contained in AP. Pure oxygen was used instead of air so that the factor of nitrogen can be excluded. XRD analysis results show that no BN crystals were found in the combustion residue. Elementary analysis further testified that the content of elemental nitrogen was lower than 0.3% and can be ignored.

It is obvious that, if boron is combusted in the atmosphere without nitrogen, no BN will be created, even if the components of the sample contains elemental nitrogen.

Effect of Air Pressure on the Output of BN

In experiment B, the relationship between BN production and air pressure was studied. According to the XRD charts, a peak height of BN (where $d = 3.33$) was measured and used to determine the amount of BN. B_2O_3 was also considered by adding all its characteristic peak heights. The results are shown in Figure 2.

The BN curve in Figure 2 indicates that the content of BN in combustion residue increases with rising air pressure, whereas the B_2O_3 curve rises first and then declines. This occurs because, when at low air pressure, the concentrations of both N_2 and O_2 are relatively low and boron is excessive. When the air pressure becomes higher, both

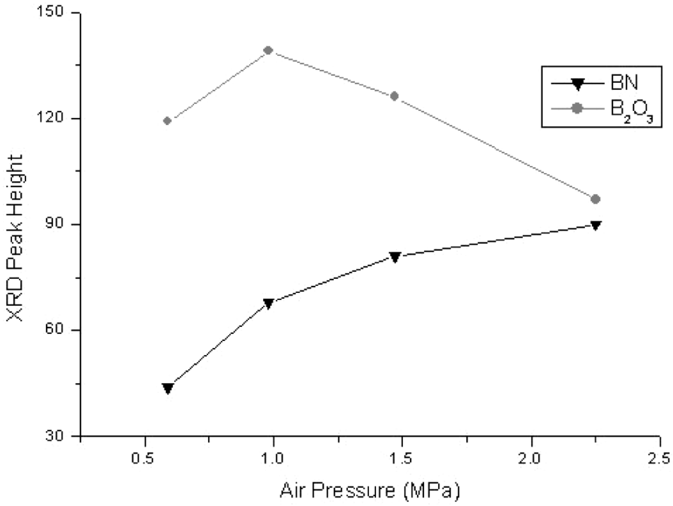

Figure 2. Relationship between BN(B_2O_3) production and air pressure.

reactions of $B + O_2$ and $B + N_2$ move toward the direction of productions because of the increasing concentrations of gaseous reactants. However, the competition of O_2 and N_2 to react with boron becomes intensified. It can be seen from the results of Figure 2 that, when both oxygen and nitrogen are ample, boron is more inclined to react with nitrogen. At the same time, oxidation of boron is restrained. This is due to the limitation of the total transformation rate of boron combustion. Thus, the increasing amount of BN in the final production will necessarily lead to the decrease of B_2O_3. From the energetic view, the creation heat of BN is far less than that of B_2O_3, which indicates the disadvantage of excessive BN production in combustion of boron-containing propellants. Therefore, we come to the conclusion that it is not efficacious for boron combustion and energy release at either too low or too high air pressure.

Effect of Coating Materials

The results of experiment C show that, although AP and KP are similar oxidizers, the combustion products of B^{AP} and B^{KP} are much different. XRD showed that, in the residue of B^{AP}, there is much B_2O_3,

Table 1
Elemental analysis results of B^{AP} and B^{KP} combustion residue

Sample	N%	BN%
B^{AP}	2.793	4.948
B^{KP}	9.731	17.238

BN, the next largest quantity, as well as some B_7O. However, the residue of B^{KP}, oxide of boron, exists as KB_5O_8, rather than B_2O_3. Some white power found is mainly KCl. In addition, BN exists, but cannot be distinguished because of the overlap of the KB_5O_8 peak and the BN peak at about $d = 3.33$. Therefore, other analysis methods are needed to detect the content of BN in residue of B^{KP} so that comparison can be made to that of B^{AP}.

Using elementary analysis to detect the elemental nitrogen percentage content in the residue is an alternative way to obtain the content of BN. The results are shown in Table 1 (It is assumed that all elemental nitrogen exists in one format, BN, which has been confirmed by the result of XPS experiment.) From Table 1 we can see that the content of BN in B^{AP} residue is not as much as that in B^{KP} residue.

XPS experiments further provide the relative content of BN and B_2O_3 in both B^{AP} and B^{KP}. Form the magnified charts of XPS we find that the peak that represents B is split into double peaks (see Figures 3 and 4). That is caused by the presence of different energy states of boron. The left peak represents B_{1s} of BN, and the right one represents B_{1s} of B_2O_3.

The quantitative analysis results of B and elemental nitrogen in B^{AP} and B^{KP} residue are shown in Table 2. Results in Table 2 show that combustion of B^{AP} creates more B_2O_3 than BN, while B^{KP} does the opposite. Thus, selection of coating oxidizers of boron has some effect on the combustion products of boron. Compared to KP, AP can release more free oxygen atoms, which are much more reactive than oxygen in the air. So it helps to promote the oxidation of boron. Meanwhile, the increase of oxygen content around boron particles necessarily leads to the relative decrease of nitrogen concentration at its surface, which effectively restrains the reaction between B and N_2. Therefore, using higher oxygen-containing material to modify boron

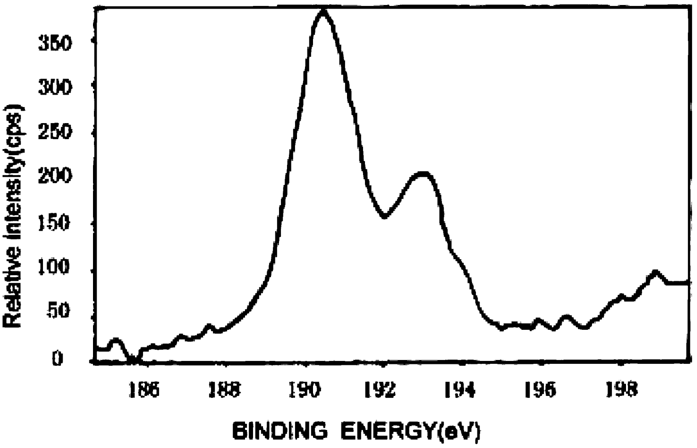

Figure 3. XPS Analysis of B_{1s} structure of B^{KP} combustion residue.

can enhance the transformation rate of boron toward B_2O_3, control the reaction between boron and nitrogen, and sequentially release more energy. In addition, the data in Table 2 show that the content ratio of N and B_1 approaches 1:1, which indicates that elemental nitrogen in the residue is mostly in the formation of BN.

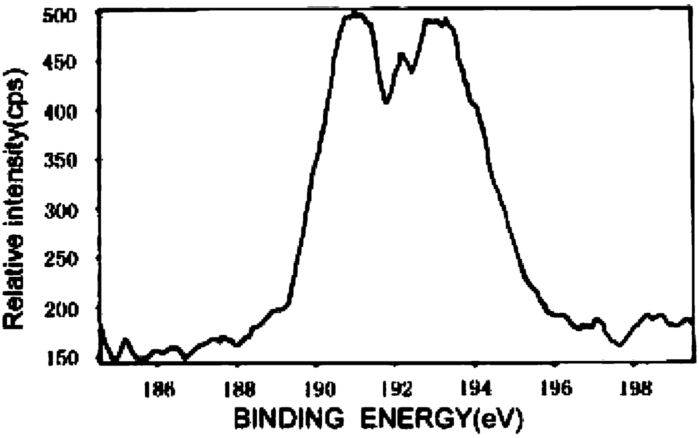

Figure 4. XPS Analysis of B_{1s} structure of B^{AP} combustion residue.

Table 2

XPS analysis of B^{AP} and B^{KP} combustion residue

Sample	N	B_1	B_2
B^{AP}	10.30	9.94	14.41
B^{KP}	14.08	14.99	7.27

Notes: B_1 represents B in BN_1, and B_2 represents B in B_2O_3.

Data in Table 2 have no dimension, which only represents the relative content of elements, not percentage content.

Conclusions

1. BN found in combustion residue of a boron-containing propellant is mainly formed by the combination of boron and nitrogen in the air, while elemental nitrogen in the component has little effect.
2. The product content of BN increases with the rising of air pressure, while B_2O_3 exhibits the tendency to increase first and then decrease.
3. Choosing high oxygen-containing material to dispose boron can restrain the formation of BN in the combustion.

Acknowledgments

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