

Effect of coating on the reactivity of boron powder

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Thermal analysis and combustion experiments were carried out to study the effect of the surface properties of boron on the thermal reaction and combustion reaction of boron and its mixture with potassium nitrate. The obtained results are as follows.

Boron powder was not completely oxidized in air because of its stable oxide layer on the surface. Fluororesin-coated boron underwent oxidation at a lower temperature, but showed a smaller fractional oxidation. Uncoated boron had a large hygroscopicity and formed boric acid if in contact with moisture. Surface coated-boron prevented the absorption of water.

The thermal reactivity and ignitability of boron-potassium nitrate mixtures were different with the composition and species of boron. Boron-rich condition caused higher thermal reactivity. The mixture that contained fluororesin-coated boron showed a lower initiation temperature of the exothermic reaction and ignition temperature than the other ones. The coating caused decrease in the linear burning rate and the drop hammer sensitivity of the mixture. For electrostatic sensitivity, the fluororesin coated-boron containing mixtures had a lower sensitivity and the epoxy resin coating showed a higher sensitivity compared to the mixture containing uncoated boron.

1. Introduction

The fuel in the pyrotechnic composition has an important role in determining its combustion characteristics. Because of its high heat yield, the boron-containing mixture has been used in igniter, primer and delay compositions, as combined with a suitable oxidizer such as red lead or potassium nitrate¹⁾. However, boron also has the disadvantage of ignition difficulty and insufficient oxidation. Moreover, the hygroscopicity must be controlled during processing because boron has a tendency to adsorb moisture from the atmosphere.

With regard to the reaction of boron with an oxidizer, there have been many reports dealing with its pyrotechnic compositions²⁾ and combustion characteristics^{3), 4), 5)}. Liu reported on the combus-

tion behavior of solid propellants for ducted rockets containing LiF-, Viton A-, silicone-coated boron⁶⁾. However, there have been few reports which dealt with the effect of the characteristics of a surface-treated boron on the reactivity and combustion characteristics of the boron-containing pyrotechnic compositions. In this study, thermal analysis and combustion experiments such as combustion calorimetry or burning rate measurements were carried out to study the effect of the surface properties of boron on the thermal reaction and combustion reaction of boron and its mixture with potassium nitrate selected as a typical oxidizer combined with boron.

2. Experimental

2. 1 Materials

The amorphous and industrial grade boron (1) (B(1)) was obtained from Kerr-McGee Chem. Co., Ltd. Its purity determined by chemical analysis using the mannitol method was 83.3 wt.%⁷⁾ and its

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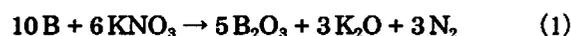
particle diameter was 2.20 μ m by a centrifugal particle size analyzer. Impurities determined by X-ray fluorescence analysis were 5.1% magnesium, 0.3% calcium and 0.9% other metals. The X-ray diffraction patterns showed the existence of a small amount of crystal boron, boric acid anhydride (B_2O_3) and boric acid (H_3BO_3). Two different borons were obtained in order to compare the effect of the type on the reactivity. One was from Hamman-Stieve Co., Ltd., (boron (2) or B(2)) and its purity was 88.5 wt.% with a particle diameter of 1.94 μ m by a centrifugal particle size analyzer. The other was from SB Chemicals Co., Ltd., (boron (3) or B(3)) and its purity was 81.3 wt.% with a particle diameter of 1.97 μ m.

Surface treatment of the boron (1) was performed using fluoro-resin Viton A and epoxy resin Epicoat 1000 dissolved in Aceton. The surface-coated boron was rotated overnight and filtered through a membrane filter followed by drying at 100 °C. The preparation condition and obtained results are shown in Table 1, in which the thickness of coating agent on the surface of boron was calculated supposing a spherical particle of boron from the following data; average particle diameter of boron is 0.46 μ m for boron (1) (Martin diameter in 3.1), densities of boron (1), Viton A and Epicoat 1000 are 1.73 g/cm³, 1.76 g/cm³, 1.17 g/cm³, respectively.

Potassium nitrate was prepared by pulverizing and sieving reagent grade material, and its average particle size was about 10 μ m.

The mixture of boron with potassium nitrate was prepared using an ordinary ball-mill mixer. The

compositions were B / KNO₃ = 4/1, 3/1, 2/1 and 1/1 by mol according to the following reaction equation:



2. 2 Analysis

The purity of boron was determined by the manitol method that after the oxidation of boron by hydrogen peroxide, the produced boric acid was analyzed by neutralization titration⁷⁾. Impurities were determined using a Shimadzu X-ray Fluorescence Analyzer XRF-1700WF. The particle size was measured using a Horiba CAPA-500 Centrifugal Particle Size Analyzer. Thermal analysis was performed with a Rigaku TAS - 200 DTA - TG Simultaneous Analyzer in argon of atmospheric pressure with a heating rate of 20 °C/min. The sample was 5 mg by weight, and was contained in an alumina cell of 5 mm high \times 5 mm Φ . The X-ray powder diffraction was performed using a Rigaku RU -200 Roter Flex. The particle morphology was observed using a Nippon Denshi JSM-2 Scanning Electron Microscope.

2. 3 Combustion experiment

The mixtures consisting of boron and potassium nitrate were burned in an aluminum cylindrical tube under atmospheric conditions, and the time for a 10-mm burning was recorded by digital memory with an optical fiber signal. The mixture was loaded nine times, and its density was 70% of the theoretical maximum density.

Table 1 Coating of boron powder by fluoro-resin (Viton A) and epoxy resin (Epicoat 1000) dissolved in acetone

Species of coating agent	Concentration of coating agent (g/1 l acetone)	Amount of adhered coating agent (g/1 g boron)	Thickness of coating agent (μ m)
Viton (1)	2.5	0.010	0.0008
	5.0	0.016	0.0012
	10.0	0.024	0.0019
	20.0	0.040	0.0032
Epicoat (1)	0.5	0.010	0.0011
	1.0	0.012	0.0013
	5.0	0.028	0.0032
	10.0	0.058	0.0070

Table 2 Chemical analysis of boron powder

Species of boron	Content of boron before washing (wt.%)	Water soluble boron (wt.%)	B ₂ O ₃ (wt.%)	H ₃ BO ₃ (wt.%)	Content of boron after washing (wt.%)
B(1)	83.3	9.0	0	9.0	91.6
B(2)	88.5	—	—	—	—
B(3)	81.3	10.3	1.5	8.8	90.6

A Shimadzu CA-4P Autocalculating Bomb Calorimeter was used to measure the heat of combustion for a 0.7-g sample under atmospheric pressure in argon.

The ignition test was carried out according to the Krupp method under argon. After the 100 mg mixture was pressed at 588 MPa, the obtained pellet was divided into 5 mg pieces before the ignition test.

2. 4 Sensitivity tests

The drop hammer test and friction sensitivity test were carried out according to the Japanese Industry Standard JIS K 4810⁹⁾. The electrostatic sensitivity test was carried out using an electrostatic sensitivity tester having fixed electrodes according to the Japanese Explosives Society Standard ES-25⁹⁾.

3. Results and Discussion

3. 1 Surface properties and the reactivity of boron powder

Table 2 shows the results of the chemical analysis of boron. As stated before, the purity of boron (1) was 83.3 wt. %. After washing with hot water, the amount of determined soluble boron (H₃BO₃, B₂O₃) was 9.0 wt% and the purity increased up to 91.6 wt. %. The amount of boric acid, which was determined by weight loss on heating to 600 °C according to the following equation, was 9.0 wt%.



On the other hand, the boric acid and the boric acid anhydride of boron (3) were 1.5 and 8.8 wt%, respectively, and the purity increased to 90.6 wt. %.

The average particle diameter of boron (1) determined by the centrifugal particle size analyzer was 2.20 μm. From the observation of the SEM

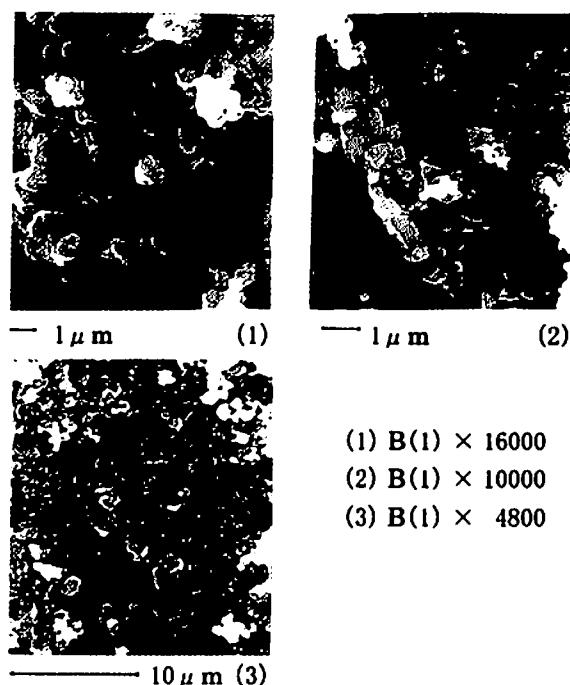


Fig. 1 SEM photographs of boron powder

photographs (Fig.1), it was noted that boron (1) consisted of primary particles of 0.1 ~ 2 μm in size and that many of the primary boron particles aggregated to form secondary particles of a few microns. It was difficult to determine the exact size of the primary particles from the SEM photographs, but average particle diameters determined from the SEM photographs (Martin diameter) were about 0.46 μm for boron (1), 0.41 μm for boron (2) and 0.45 μm for boron (3).

Figure 2 shows the ESCA spectra of the boron powder. The ESCA spectra of boron (2) show the existence of carbon and fluorine. Therefore, it was concluded that it was coated by one kind of fluororesin. Borons (1) and (3) had peaks at 192 ~ 193 eV caused by the boric acid and boric acid anhydride, but boron (2) did not have any peak at this energy level.

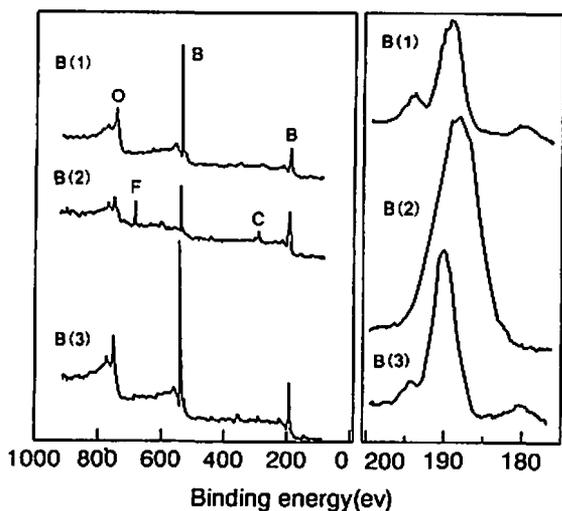


Fig. 2 ESCA spectra of boron powder

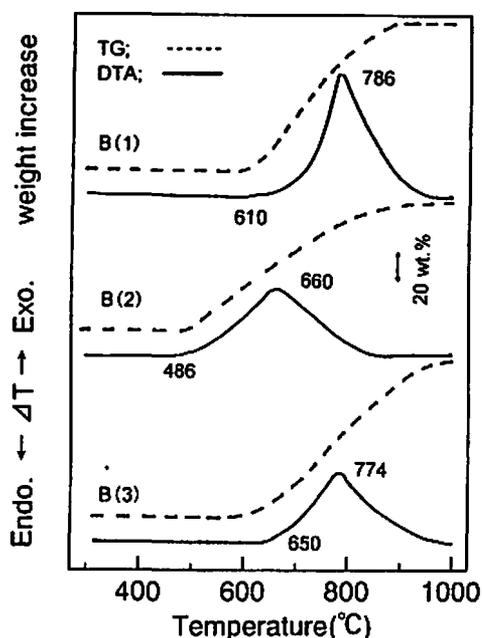


Fig. 3 DTA (solid line) and TG (dotted line) curves of boron powder in air

Figure 3 shows the DTA (solid line) and TG (broken line) curves of boron powder in air. Boron (1) was oxidized in air at temperatures ranging between 610 ~ 860 °C. The weight increase at 860 °C was about 120%. The weight increase of pure boron is 222 % for complete oxidation according to equation 3, therefore, this result corresponds to a 54% oxidation of total boron if the oxidation of the impurities is ignored:



Boron (3) showed a similar thermal behavior to

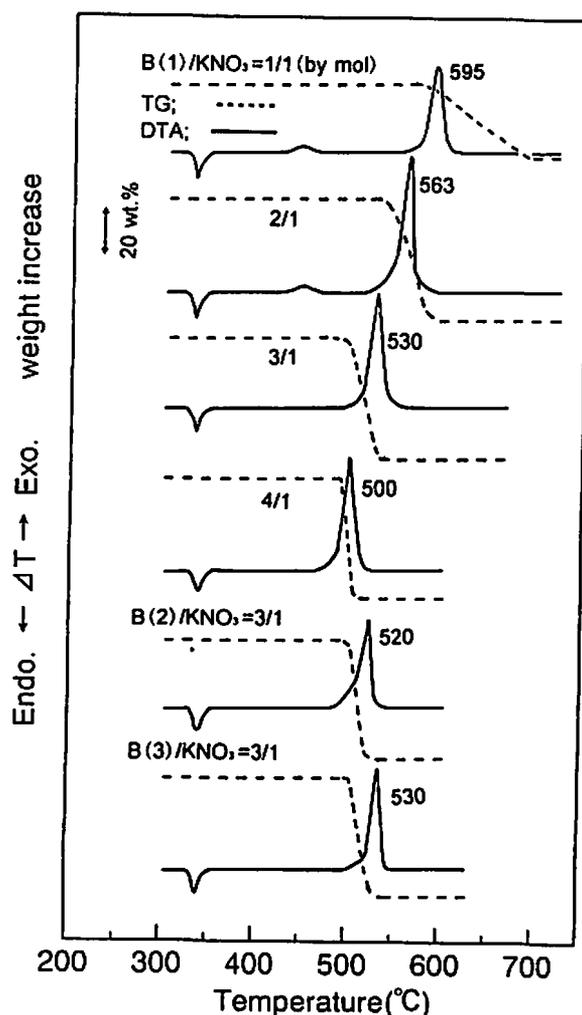


Fig. 4 DTA (solid line) and TG (dotted line) curves of boron - KNO₃ mixtures in Ar

B(1) upon heating in air and the fractional oxidation at 1000 °C was 56%. On the other hand, the oxidation of boron (2) commenced at 486 °C, which was about 130 °C lower compared to that of boron (1). However, its fractional oxidation remained at 47% at 1000 °C.

Figure 4 shows the DTA (solid line) and TG (broken line) curves of various boron-potassium nitrate mixtures in Ar. With regard to boron (1), every composition caused an intense exothermic reaction ranging between 475 ~ 610 °C. However, the thermal reactivity was different for each composition and boron-richer condition showed higher reactivity. This phenomenon may be ascribed to the difficult oxidation of boron. The boron (3)-potassium nitrate mixture also showed the same thermal behavior as that of boron (1). However, in the case of boron (2), the reaction temperature was

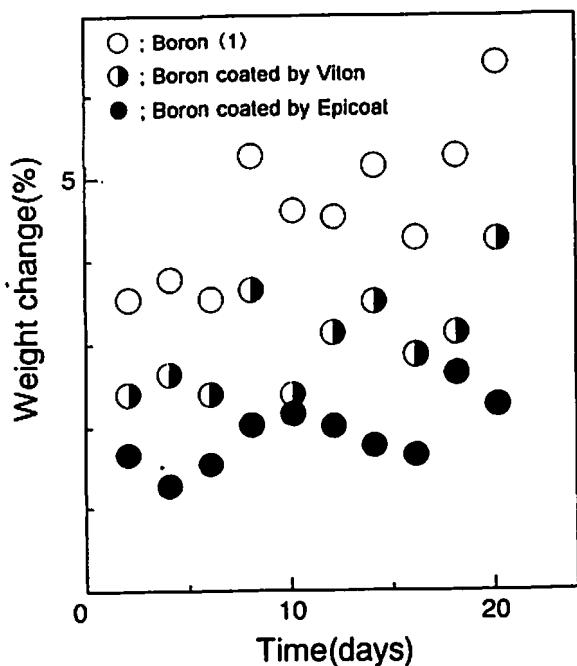


Fig. 5 Weight increase of boron powder under relative humidity of 100% at 25 °C

somewhat lower compared to the others though the exothermic peak was small.

3. 2 Effect of coating on the reactivity of boron powder

Figure 5 shows the weight increase of boron powder under a relative humidity of 100% at 25 °C. Boron (1) without coating had a large hygroscopicity and acquired 6.5% of weight increase after 20 days. This was the reverse reaction of equation (2) and the acquired water was removed upon heating up to 600 °C. The boron coated by Viton A showed 4.2 % of weight increase and that 2.2% by Epicoat 1000. From these results, the coating had some effect on the boron that prevented the absorption of water. The mechanism of the water adsorption was not examined in this experiment. However, adsorption may occur through the mechanism that oxygen and water which diffuse through the physically or chemically adsorbed layer react unreacted boron.

Figure 6 shows the results of the DTA and TG curves of Viton A, Epicoat 1000 and their mixtures with potassium nitrate in argon. Viton A underwent endothermic decomposition at in the temperature range of 420 ~ 490 °C. Epicoat 1000 underwent a two-step decomposition showing endothermic peak ranging between 420 ~ 490

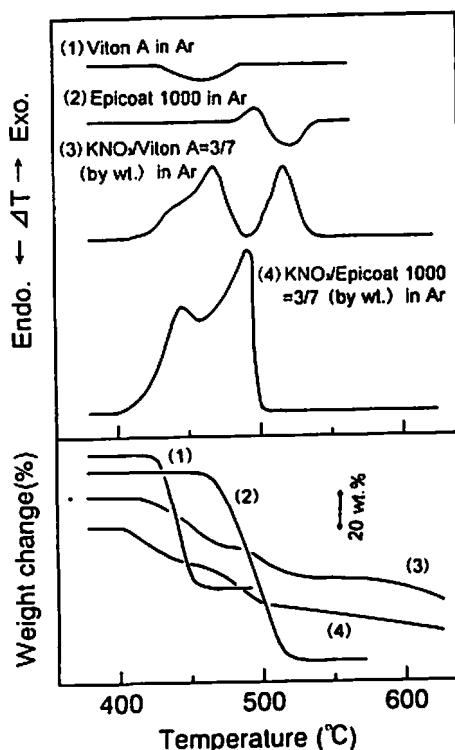


Fig. 6 DTA and TG curves of Viton, Epicoate and their mixtures with KNO_3

°C and endothermic between 480 ~ 510 °C. The mixture of the Viton A with potassium nitrate underwent a two-step exothermic reaction at the temperatures ranging between 410 ~ 490 °C and between 490 ~ 540 °C. The mixture of Epicoate 1000 with potassium nitrate showed an exothermic reaction at the temperatures ranging between 400 ~ 510 °C.

From the thermal analysis of the coated boron in air, Viton A-coated boron showed a similar thermal behavior to boron (2) and there was no difference in the thermal reactivity between boron without a coating and the Epicoat 1000 coated one. Figure 7 shows the effect of the surface coating of boron on the thermal reactivity of the mixtures of boron with potassium nitrate in argon. The mixture that contained the Viton A-coated boron underwent an exothermic reaction at a temperature lower than that for the mixture without coating. On the other hand, the reaction temperature of the mixture with Epicoat coated boron was similar compared to that for the mixture containing uncoated boron.

Figure 8 shows the results of the linear burning rate of boron - potassium nitrate mixtures under atmospheric conditions. The linear burning rate

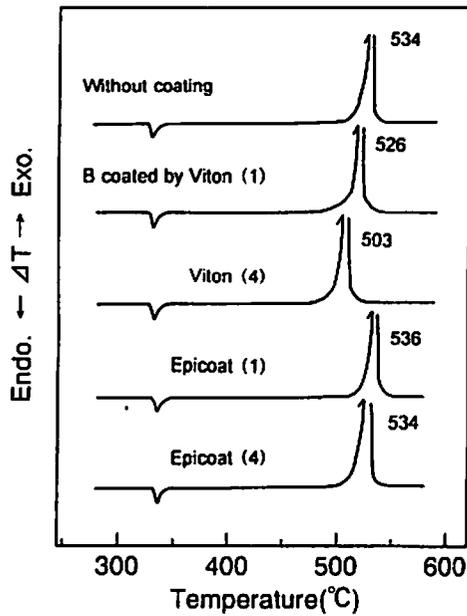


Fig. 7 DTA curves of the mixtures of surface coated boron with KNO_3

decreased with the increase of the amount coated by Viton A and Epiccoat 1000. However, the heat of combustion remained constant with the increase of the amount of Viton A and Epiccoat coating agent, having the values of 6310 ~ 6410 J/1g mixture for the composition of B/ KNO_3 = 3/1 by mol.

Table 3 shows the results of the drop hammer test of boron-potassium nitrate mixtures, in which drop hammer sensitivity is represented by the height causing one firing out of 6 trials (1/6 explosion point). The different compositions of the mixtures

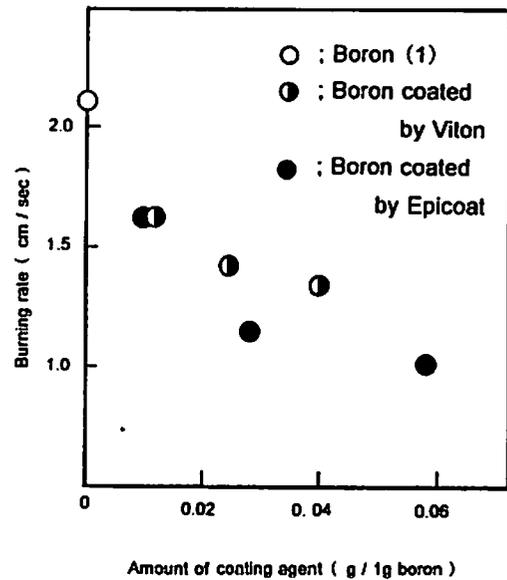


Fig. 8 Linear burning rate of boron - KNO_3 mixtures under atmospheric conditions

containing uncoated boron (1) had the same drop hammer height of 30 ~ 40 cm and are classified as class 6 in JIS. The drop hammer height for the mixture containing boron (3) was 20 ~ 30 cm, showing a little higher sensitivity. On the other hand, the boron (2) coated by the fluororesin containing mixture had a lower sensitivity of the 40 cm drop hammer height. The Viton A-coated boron containing mixtures decreased in drop hammer sensitivity with increasing amount of Viton A and that with the maximum amount of coating became insensitive. The Epiccoat 1000 coating also had the

Table 3 Drop hammer test results of boron - KNO_3 mixtures

Sample (composition) (by mol)	B(1)/ KNO_3			B(2)/ KNO_3	B(3)/ KNO_3
	4/1	3/1	2/1	3/1	3/1
1/6 explosion point (cm)	30~40	30~40	30	40	20~30
Class of sensitivity in JIS	6	6	6	7	5
Sample B coated by Viton	B coated by Viton/ KNO_3 = 3/1 (by mol)				
	(1)	(2)	(3)	(4)	
1/6 explosion point (cm)	30~40	40~50	30	—	
Class of sensitivity in JIS	6	7	6	8	
Sample B coated by Epiccoat	B coated by Epiccoat/ KNO_3 = 3/1 (by mol)				
	(1)	(2)	(3)	(4)	
1/6 explosion point (cm)	20~30	30~40	30~40	—	
Class of sensitivity in JIS	5	6	6	8	

Table 4 Electrostatic sensitivity of boron - KNO₃ mixtures

Sample	B(1)	B(1)	B(2)	B(3)	B coated by Viton(2)	B coated by Viton(3)	B coated by Epicoat(2)
Composition B/KNO ₃ (by mole)	4/1	3/1	3/1	3/1	3/1	3/1	3/1
1/10 explosion point (mJ)	71	60	45	45	60	115	10
Class of sensitivity in JIS	4	4	4	4	4	4	3

same effect as Viton A coating.

Table 4 shows the results of the electrostatic sensitivity test of the boron-potassium nitrate mixtures, in which electrostatic sensitivity are represented by the energy causing one firing among ten trials (1/10 explosion point). The different compositions of the mixtures containing uncoated boron had a similar ignition energy (1/10 explosion) of 45 ~ 71 mJ which was classified as class 4 of the Japan Explosives Society Standard. On the other hand, the Viton A-coated boron containing mixtures had a larger ignition energy of 60 ~ 115 mJ and the Epicoat 1000 coating had a smaller value compared to the mixture containing uncoated boron. Friction sensitivity is an important factor for its safe production. Every composition of boron - potassium nitrate was insensitive in the friction sensitivity test even under the maximum applied load of 36 kgf.

It is known that an Arrhenius type equation described by equation (4) exists between the delay time t and temperature T for the ignition test:

$$\ln t = E_a/RT + \ln A \quad (4)$$

Plots of ignition delay time t and $1/T$ gave a straight line and the activation energy was obtained from the slope of the plots. Table 5 shows the results of the Ignition tests for boron-potassium nitrate mixtures. The mixtures containing uncoated boron and that coated by Epicoat had the minimum ignition temperatures of 490 °C and 484 °C, and the temperature at which the delay time was 4 sec ($T_{4\text{sec}}$) was 554 °C and 582 °C, respectively. On the other hand, the mixture containing the Viton A-coated boron had a lower ignition temperature

Table 5 Ignition tests results of boron - KNO₃ (B/KNO₃ = 3/1 by mole) mixtures

Sample of B	B(1)	B coated by Viton(4)	B coated by Epicoat(4)
T_{\min}	490	450	484
$T_{4\text{sec}}$	554	530	582
E_a (kJ/mol)	85	61	102

T_{\min} : Minimum ignition temperature (°C), $T_{4\text{sec}}$: Ignition temperature at which delay time is 4 seconds, E_a : Activation energy for ignition

and smaller activation energy for ignition. As the detailed reaction mechanism of the mixture containing coated boron was not examined in this experiment, the exact reason for the effect of coating agents on the thermal reaction and combustion was not clarified, but this may be interpreted as follows. It is well known that fluorine undergoes glassification when reacting with boron, this may be weakened the steady oxide layer on the boron surface thus making the initiation of the reaction occur easier. However, after the oxidation proceeds to some extent, the glassified layer acts against further oxidation and may eventually cause a lower fractional oxidation.

4. Conclusions

Boron powder was oxidized in air at temperatures ranging between 610 ~ 860 °C, but its complete oxidation was not attained because of its stable oxide layer on the surface. Boron without a coating had large hygroscopicity and absorbed water to form boric acid if left in contact with moisture, and the surface coated-boron prevented the absorption of

water to some extent. The fluoro-resin-coated boron underwent oxidation at a lower temperature, but showed a smaller fractional oxidation at higher temperatures.

The thermal reactivity and ignition temperature of the boron-potassium nitrate mixtures were different based on the composition and species of boron. That is, a boron-rich condition had a higher thermal reactivity, and the mixture that contained the Viton A-coated boron showed a lower initiation temperature of the exothermic reaction and ignition temperature than the others. Coating caused decrease in the linear burning rate and decrease of the drop hammer sensitivity of the mixture. With respect to electrostatic sensitivity, the Viton A-coated boron containing mixtures had larger ignition energy (1/10 explosion) of 60 ~ 115 mJ and the Eicoat 1000 coated boron had a smaller value compared to the mixture containing uncoated boron. Anyway, what kind of property is desired is important factor to select coating agent of boron.

References

- 1) J. A. Connkling, "Chemistry of Pyrotechnics", Marcel Dekker, (1985) p. 72
- 2) U. S. Army Armament Research and Development Command, "A Compilation of Hazard and Test Data for Pyrotechnic Compositions, (1980) p. 211~392
- 3) H. YANO, J. of Japan. Explo. Soc., 49(2), 129 (1988)
- 4) K. HASUE, M. MATSUKAWA and H. TAMURA, J. of Japan. Explo. Soc., 60(1), 10(1999)
- 5) K. HASUE, M. MATSUKAWA and H. TAMURA, J. of Japan. Explo. Soc., 60(1), 17(1999)
- 6) Tai-Kang Liu, Song-Ping Luh and Huey-Cherng Perrng, Propell. Explos. Pyrotech., 16, 156(1991)
- 7) S. Kato, Bull. Chem. Soc. Japan, 83, 1039 (1962), JIS K 8863
- 8) JIS K 4810, Japanese Standards Association (1979)
- 9) Japan Explosives Society Standard, ES-25, Japan Explosives Society(1988)

ホウ素の反応性に及ぼす表面被覆の影響

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フッ素樹脂やエポキシ樹脂で表面を被覆した場合などを含むホウ素の表面物性が、ホウ素単体やその硝酸カリウムとの混合物の熱反応性や燃焼反応性に及ぼす影響を、表面物性の測定、熱分析および燃焼実験などにより検討した。

ホウ素単体は、空気中での酸化では、その安定な酸化被膜のために完全には酸化されない。フッ素樹脂で表面を被覆した場合にはより低温で酸化反応は起こるが、酸化率はむしろ低下する。表面被覆しないホウ素は吸湿性を持ち、吸湿の結果ホウ酸を生成する。ホウ素を表面被覆すると、吸湿性はある程度低下させることができる。

ホウ素とその硝酸カリウムとの混合物の熱反応性や燃焼反応性は、混合物の組成やホウ素の種類により異なった。すなわち、混合物中のホウ素量が多くなると熱反応性は高くなった。フッ素樹脂で表面を被覆したホウ素は他のもので被覆されたものに比較して、混合物の熱反応の温度を低下させ、また、燃焼反応では発火温度を低下させた。いずれの表面被覆剤で被覆しても、硝酸カリウムとの混合物の燃焼速度は低下し、落つい感度試験での感度は鈍感化した。これに対して、表面被覆しない場合に比較して、静電気感度試験ではフッ素樹脂で表面を被覆した場合には感度は鈍感化した。エポキシ樹脂で表面を被覆した場合にはむしろ鋭感化した。摩擦感度試験ではいずれも不爆であった。

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