

Thermal reaction and combustion reaction of boron - cupric oxide mixture

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In this study, thermal analysis and combustion experiments, such as combustion calorimetry or the measurement of burning rate and combustion temperature were carried out to clarify the thermal reaction and combustion reaction of boron - cupric oxide mixture. The results obtained are as follows :

The mixture of boron with cupric oxide caused an intense exothermic reaction, but the thermal reactivity was different with the shape and the composition of the sample in which a boron-rich condition showed higher thermal reactivity. The linear burning rate, heat of combustion and combustion temperature of boron - cupric oxide mixture had the maximum value at fuel-rich condition of the equimolar composition. The pressure effect was also recognized with regard to the linear burning rate and heat of combustion. The fractional oxidation of boron for the combustion at atmospheric pressure was 81 ~ 83% for stoichiometric and oxidizer-rich conditions. Under pressurized conditions, it increased with increasing ambient pressure and amount of oxidizer, and a complete oxidation of boron was attained at the oxidizer-rich and pressurized composition.

1. Introduction

Boron (B) is a stable material because of its high melting point and stable surface oxide layer. However, boron can produce a good heat output due to its high exothermicity per unit gram, if well burned¹⁾. Therefore, combined with high melting point oxidizing agents, a boron can be expected to have both high heat-resistant and exothermic characteristics. Ordinarily, a pyrotechnic composition which contains boron as fuel cannot produce whole capable heat output, because the stable surface oxide layer (B_2O_3) demonstrates the resistance to chemical reaction. This oxide, similar to silicon dioxide, has a solid acidic nature. Therefore, a solid basic substance such as oxides of alkaline earth metal is selected as an oxidizing agent, this composition can be expected to display enough reactivity to cause a perfect oxidation.

Boron-containing pyrotechnic compositions, such as

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boron-red lead, potassium nitrate, barium chromate or lead oxide, are utilized as delay mixture, igniter mixture and primer mixture²⁾. With regard to the reaction of boron with oxide, it was reported that doped oxide exhibited high reactivity³⁾. On the other hand, there have been few reports which deal with the boron - cupric oxide (copper (II) oxide, CuO) mixture, because it is not so popular in practical use as pyrotechnics. This composition is expected to have both high heat-resistant and high exothermic characteristics. In this study, thermal analysis and combustion experiments such as combustion calorimetry or burning rate measurement were carried out to clarify the thermal reaction and combustion reaction of amorphous boron - cupric oxide mixture.

2. Experimental

2.1 Materials

The sample boron (B) was amorphous and reagent grade obtained from Degussa JAPAN Co., Ltd. Its declared purity is 90 ~ 92wt.%, but the one determined by chemical analysis using mannitol method was 87.9wt.%⁴⁾. Impurities determined by X-ray fluorescence analysis were 3.0% magnesium, 0.5% iron

and 0.2% copper. X-ray diffraction patterns showed the existence of a small amount of crystal boron, anhydrous boron oxide (B_2O_3) and boric acid (H_3BO_3). After washing soluble boron with hot water, the purity increased up to 90.8wt%. An average particle diameter determined by centrifugal particle size analyzer was $4.62 \mu m$. From the observation of SEM photographs (Fig. 1-a), it was noted that boron consisted of primary particles of $0.1 \sim 2 \mu m$ in size and that about a dozen of the primary boron particles aggregated to form a secondary particle of a few microns. It was difficult to determine the exact size of the primary particle from SEM photographs, but its average particle diameter was under about $1 \mu m$.

Cupric oxide was reagent grade and had a purity of 97.9wt.% based on iodometry. From SEM observation (Fig. 1-b), the cupric oxide was likely to be a single crystal and consisted of $0.5 \sim 7 \mu m$ particles in size.

The mixture of boron with cupric oxide was prepared using an ordinary ball-mill mixer. The composition was boron/cupric oxide = 1/0.5, 1/1, 1/1.5, 1/2, 1/3 by mole, which were intended to cover fuel-rich (1/0.5, 1/1), equimolar (1/1.5) and oxide-rich conditions (1/2, 1/3), according to the following reaction equation :



2.2 Analysis

The purity of boron and unreacted one in the mixture were determined by the method of mannitol, in which after oxidation of boron by hydrogen peroxide,

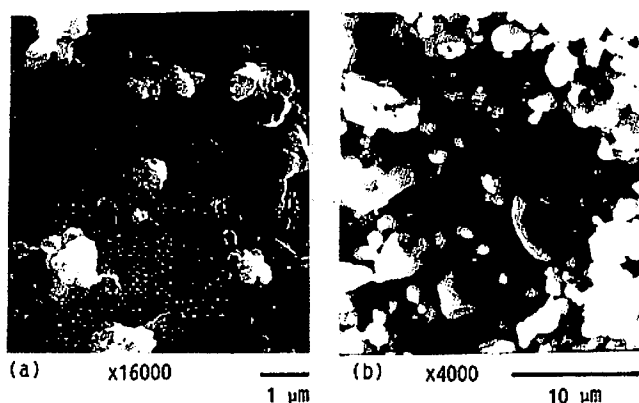


Fig. 1 SEM photographs of boron (Fig. 1-a) and cupric oxide (Fig. 1-b)

the produced boric acid was analyzed by neutralization titration. Impurities were determined by a Shimadzu X-ray Fluorescence Analyzer XRF-1700WF. The particle size was measured using a Horiba Centrifugal Particle Size Analyzer CAPA-500. Thermal analysis was performed with a Rigaku DTA - TG Simultaneous Analyzer TAS-200 in argon under pressurized or atmospheric conditions with a heating rate of $20^\circ C/min$. Sample weight was 5 mg, and the sample container was a cell of 5mm high \times 5mm ϕ made of alumina. X-ray powder diffraction was performed using a Rigaku Roter Flex RU-200. The particle morphology was observed using a Nippon Denshi Scanning Electron Microscope JSM-2.

2.3 Combustion experiment

The delay mixtures consisting of B-CuO were burnt in an aluminum cylindrical tube under argon pressurized or atmospheric conditions, and the time for 10-mm burning was recorded using digital memory with optical fiber signal. The delay powder was loaded nine times, and its density was 70% of the theoretical maximum density. The combustion temperature was measured with a W/W-Re thermocouple using a Digital Scope DL708 of Hokushin Denki Co., Ltd.

A Shimadzu Autocalculating Bomb Calorimeter C-3 was used to measure the heat of combustion for a 0.7-g sample under pressurized and atmospheric condition in argon.

3. Results and Discussion

3.1 Thermal reactivity of the mixture of boron with cupric oxide

Fig. 2 shows the TG and DTA curves of boron in air. Boron was oxidized in air at temperatures ranging between 555 and $855^\circ C$. Weight increase at $855^\circ C$ was about 65%. On the other hand, the weight increase of pure boron being 126% for complete oxidation according to equation 2, this result corresponded to 59% oxidation of total boron if the oxidation of impurities was ignored.



The melting point of cupric oxide is $1026^\circ C$, and the thermal analysis of cupric oxide in argon did not show any reactions below $900^\circ C$.

Fig. 3 shows the DTA curves for various composi-

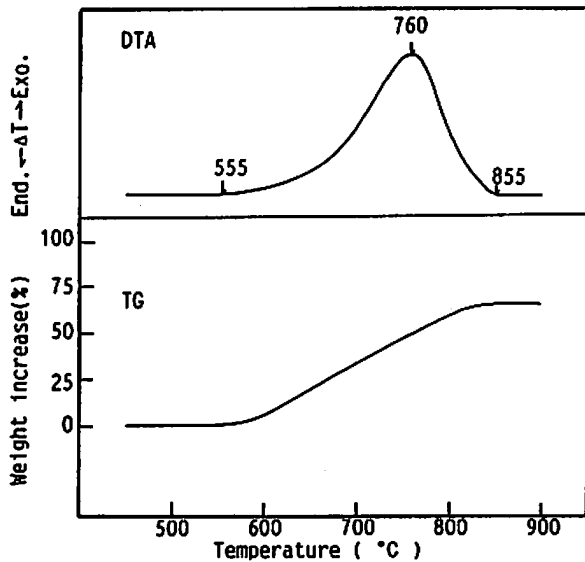


Fig. 2 TG and DTA curves of boron in air

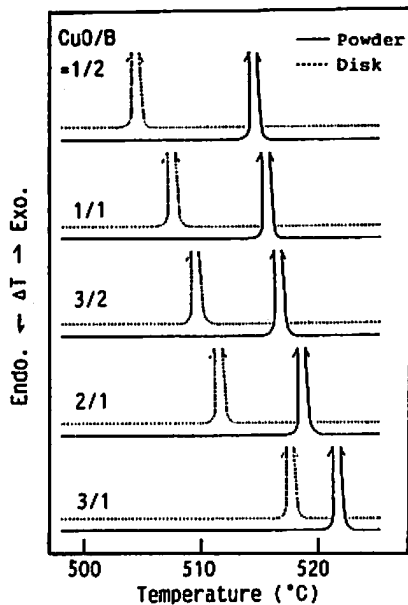


Fig. 3 DTA curves of boron - CuO mixtures in the form of powder (solid line) and pelletized shape

tions of boron - cupric oxide mixtures under atmospheric pressure of argon. Every composition caused an intense exothermic reaction at temperatures ranging between 504 and 521 °C, but the thermal reactivity was different with the composition and the shape of the sample. In the case of a pelletized shape (disk, dotted line) which was shaped by pressing, an exothermic reaction occurred at lower temperature compared to the powder form (solid line), because of intimate contact. With regard to composition, a boron-

rich condition showed higher reactivity. These phenomena can be ascribed to a difficult oxidation of boron and the difference in particle size of boron and cupric oxide.

The thermal reactivity was also affected by the surrounding pressure. Fig. 4 shows the effect of the pressure on DTA curves for the stoichiometric composition of boron - cupric oxide mixtures. The decomposition temperature showed a lowering of 34 °C at pressurized condition of 10.1MPa (100atm) compared to that at atmospheric ones. Because pure solid-state reaction should not be affected by the surrounding pressure or reaction species in the gas phase, it can be deduced that the reaction of boron - cupric oxide mixtures did not proceed completely through a solid-state reaction.

3.2 Combustion characteristics of boron - cupric oxide mixture

Fig. 5 shows the linear burning rate of boron - cupric oxide mixtures under atmospheric conditions. The linear burning rate had the maximum value at the equimolar composition. The composition which had the maximum value of the linear burning rate was different from that for the highest thermal reactivity, but was under fuel-rich conditions. These phenomena can be ascribed to a difficult oxidation of

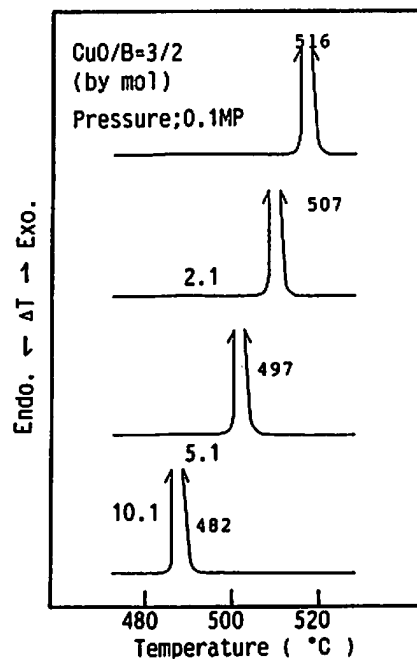


Fig. 4 Effect of the pressure on DTA curves of boron - CuO mixtures

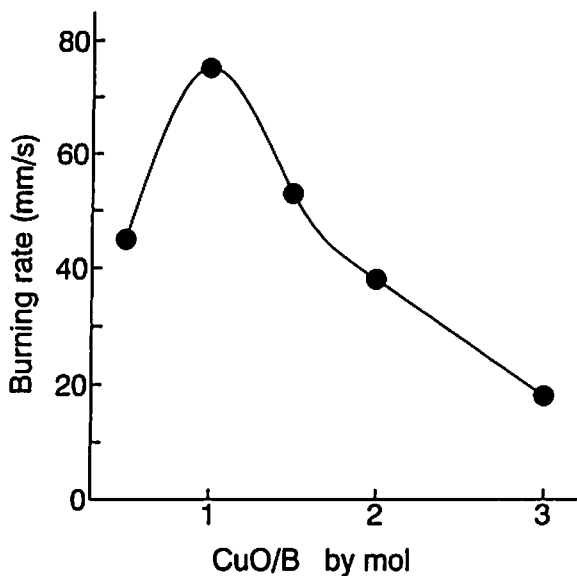


Fig. 5 Linear burning rate of boron - CuO mixtures under atmospheric conditions

boron, the difference in particle size and the difference in the thermal reactivity or thermal diffusivity. From these considerations, the surface combustion is considered to have a very important role to propagate the combustion wave of boron-cupric oxide mixtures.

Fig. 6 shows the linear burning rate of boron - cupric oxide mixtures under pressurized conditions. The linear burning rate increased with increasing ambient pressure. In propellant combustion, the linear burning rate under pressurized conditions V is represented by the following Vieille's equation :

resented by the following Vieille's equation :

$$V = bP^n \quad (3)$$

where P is the pressure, n is the pressure index and b is a constant. The pressure index n was 0.09, 0.10 and 0.05 for boron/cupric oxide = 0.5/1, 1.5/1 and 3/1 by mole, respectively. The small pressure index was ascribed to the fact that the main combustion reaction is a solid-state reaction.

As the detailed combustion mechanism was not examined in this experiment, the exact reason for the pressure effect on combustion characteristics was not clarified. From the observation of the combustion wave, it was noted that the unreacted boron in the condensed phase burned in the flame zone in the gas phase. In the combustion wave, the heat was fed back from the gas phase to the condensed phase. Therefore, the pressure effect can be ascribed to the fact that this flame zone existing near the condensed phase was shortened and that the heat flux sent from the flame zone became larger under pressurized conditions.

Fig.7 shows the combustion temperature of boron - cupric oxide mixtures at atmospheric pressure. The combustion temperatures for the oxidizer - rich condition decreased, and the maximum temperature was obtained at the equimolar composition. However, the combustion temperature had approximately the same values between the fuel rich (boron/cupric oxide =

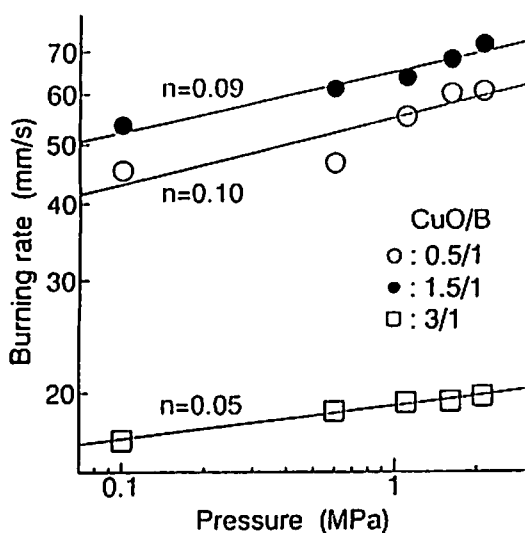


Fig. 6 Linear burning rate of boron - CuO mixtures under pressurized conditions

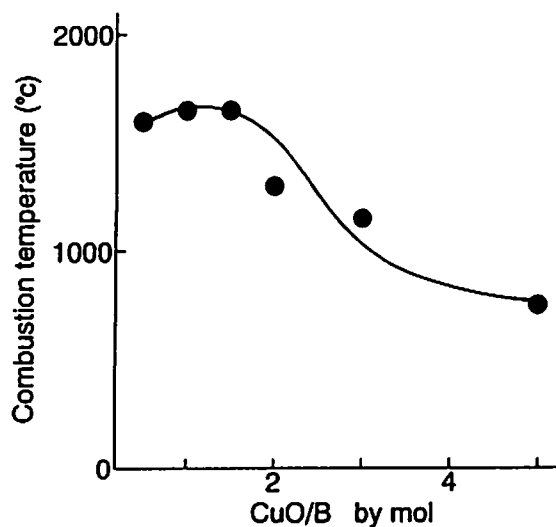


Fig. 7 Combustion temperature of boron - CuO mixtures under atmospheric pressure

0.5/1 by mole) and stoichiometric conditions (boron /cupric oxide = 1.5/1).

3.3 Fractional oxidation of boron for the mixtures of boron with cupric oxide

Fig. 8 shows the heat of combustion of boron - cupric oxide mixtures under atmospheric and pressurized conditions of argon. The heat of combustion had the maximum value at the equimolar composition under both atmospheric and pressurized conditions. Moreover, the pressure effect was also recognized showing that the heat of combustion under pressurized conditions had a greater value compared with that under atmospheric conditions.

Fig. 9 shows the X-ray diffraction patterns of the reaction residue after the combustion of various compositions for boron - cupric oxide mixtures under atmospheric conditions. From the observation of X-ray powder diffraction, reaction residues did not contain any compounds of boron, because of its amorphous structure. In addition to this, copper alone was recognized only in the combustion residue of the fuel-rich composition of boron/cupric oxide = 0.5/1 by mole. Another fuel-rich condition of equimolar composition contained metal copper and cuprous oxide (Cu_2O), which showed that cupric oxide cannot be thoroughly reduced even under fuel-rich conditions. Oxidizer-rich conditions also showed the residues of both copper and cuprous oxide.

Fig.10 shows the fractional oxidation of boron after the combustion of boron - cupric oxide mixtures under

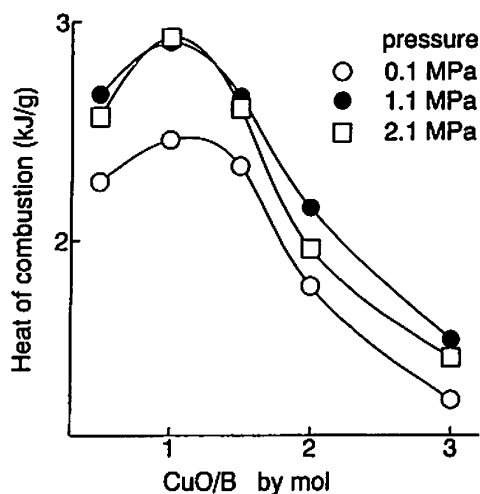


Fig. 8 Heat of combustion of boron - CuO mixtures under various pressures of argon

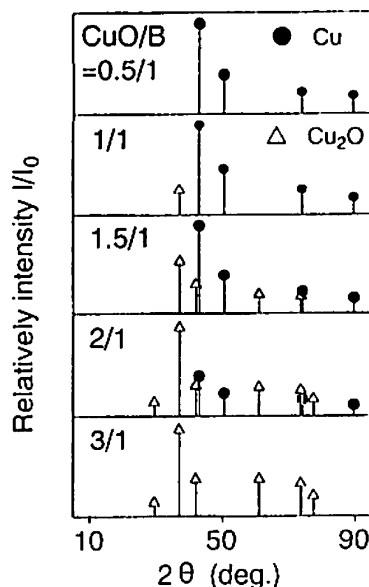


Fig. 9 X-ray powder diffraction patterns for the combustion residue of various compositions of boron - CuO mixtures

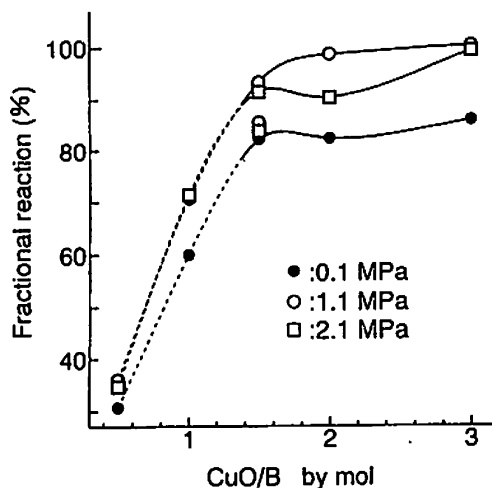


Fig. 10 Fractional reaction of boron in the combustion of boron - CuO mixtures

atmospheric and pressurized conditions of argon. In this figure, the dotted line (left-hand side of stoichiometric composition) indicated the results for fuel-rich composition, and solid line (right-hand side) those for the oxidizer-rich composition. The fractional oxidation of boron at atmospheric pressure was 81% for stoichiometric conditions and remained almost unchanged with increasing amount of oxidizer. Under pressurized conditions, it increased with increasing ambient pressure and oxidizer condition, and a complete oxidation of boron was finally attained for the

oxidizer-rich composition of boron/cupric oxide = 3/1 by mole at 1.1 and 2.1MPa.

4. Conclusions

From the experiments of thermal reactivity, the mixture of boron with cupric oxide caused an intense exothermic reaction at temperatures ranging over 504 ~ 521 °C, but the thermal reactivity was different with the composition and the shape of the sample. With regard to composition, a boron-rich condition showed high thermal reactivity.

The linear burning rate of the boron - cupric oxide mixture had the maximum value at fuel-rich conditions of the equimolar composition, which was different from that for the highest thermal reactivity. The linear burning rate under pressurized conditions increased with increasing ambient pressure. However, the pressure index was a small value of 0.05 ~ 0.10. The heat of combustion and the combustion temperature for the boron - cupric oxide mixture had the same tendency as the linear burning rate which was affected by composition and ambient pressure. Moreover, from a difficult oxidation and high thermal diffusivity of boron, a surface combustion is very impor-

tant factor in the propagation of the combustion wave.

None of the compounds which contained boron was recognized in the reaction residue, because of its amorphous structure. Metal copper and cuprous oxide were produced for fuel-rich, stoichiometric and, furthermore, even for oxidizer-rich conditions.

The fractional oxidation of boron under atmospheric pressure was 81 ~ 83% for stoichiometric and oxidizer-rich conditions. Under pressurized conditions, it increased with increasing ambient pressure and the amount of oxidizer, and a complete oxidation of boron was attained for the oxidizer-rich composition 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)pp.211 ~ 392
- 3) J.H.McLain, "Pyrotechnics," The Franklin Institute Press (1980) p.39
- 4) S. Kato, Bull. Chem. Soc. Japan, 83, 1039 (1962) JIS K 8863

ホウ素 - 酸化銅混合物の熱反応および燃焼反応

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ホウ素と酸化銅の混合物は激しい発熱反応を示すが、その反応性は試料の形状や組成によって異なった。その際に、特にホウ素過剰の条件で高い反応性を示した。ホウ素 - 酸化銅混合物の燃焼速度、燃焼熱および燃焼温度はホウ素過剰の条件下で最高値を示した。燃焼反応に及ぼす圧力の影響も認められた。

燃焼反応でのホウ素の反応率は、大気圧下、等量または酸化剤過剰の組成では81 ~ 83%であった。加圧下では、圧力および酸化剤の量とともに酸化率は上昇し、酸化剤過剰でかつ2.1MPaの条件で完全に酸化された。

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